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SHAPE-SELECTIVE METHYLATION OF *meta*-CRESOL

by

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Synopsis

Phenol, cresols and xyenols are of enormous industrial importance, mainly in the polymers (resins), electronics, pesticides, pharmaceutical, paint and dye industries.

The selective production of cresols and xyenols is difficult, partly owing to the number of different isomers that occur and, since many of these isomers have similar boiling points, separation via distillation is not in all cases effective or economical. Other separation techniques are often complicated and costly. Consequently, the direct selective synthesis of individual isomers is to be technically highly prized.

In this work the synthesis of specific xylenol isomers was investigated via acid catalysed methylation of *m*-cresol with methanol, and focusing on shape-selective or potentially shape-selective zeolites and the effects of varying reaction parameters. Attention was drawn to specifically producing the "slim" isomers, 2,5-xyleneol and 3,4-xyleneol. Regular commercial catalysts based on zeolites FER, MFI, MOR, MTW and BEA were applied. Results are compared to product distributions obtained over non shape-selective, amorphous silica-alumina.

It was found that at 300°C, 'O' alkylation to 3-methylanisole and 'C' alkylation to 2,5-, 3,4- and 2,3-xyleneol occurred as parallel primary reactions, with the former dominating at about 60 % selectivity. In subsequent reactions, 3-methylanisole is consumed (mainly via further alkylation) while the three primary xyleneol products are comparably stable, just undergoing some 1,2-shift isomerisation. Of the reaction conditions, space velocity, pressure and methanol : *m*-cresol feed ratio had only an indirect effect on selectivity via conversion, while temperature had an additional effect on selectivity, beyond its effect on conversion, driving isomer distributions towards the thermodynamic equilibrium.

Observed product shape-selective effects were minor - in the xyleneol fraction just showing a small effect over zeolites FER and MOR, favouring the "slim" 2,5-xyleneol isomer. Within the trimethylphenols, the "slim" 2,4,5-isomer was favoured over MFI zeolites.

It is evident that the typical industrial catalysts, consisting of zeolites of small crystal size between 0.1 – 0.2 µm, do not effect product shape selectivity in the *m*-cresol methylation reaction.

It is recommended that catalysts be applied whose zeolitic constituents are able to enhance the Thiele Modulus of the *m*-cresol methylation reaction by either or all of high aluminium content, large crystal size or partially blocked pore systems.

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Glossary

Symbol	Description
Al	Aluminium
Al ₂ O ₃	Alumina
BEA	Zeolite β
BHT	2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol
Bi	Bismuth
Ce	Cerium
CH ₄	Methane
C _i	Relative distribution of species i in a specified group of species (i.e. 2,5-xylenol within total xylenol product)
CM DX	Cresol methylation, experiment run number X
CO	Carbon oxide
CO ₂	Carbon dioxide
COD	Conversion of olefins to diesel
Co	Cobalt
Cr	Chromium
Cu	Copper
DPE	Diphenylether
DME	Dimethylether
FER	Zeolite Ferrierite
FCC	Fluidised catalytic cracker
FIC	Flow indicator and controller
FID	Flame ionisation detector
Ga	Gallium
GC	Gas chromatograph / gas chromatogram
Ge	Germanium
HCl	Hydrochloric acid
HDN	Hydrodenitrogenation
HDS	Hydrodesulphurisation
HF	Hydrofluoric acid
H ₂ O	Water
HPLC	High pressure liquid chromatography
H ₃ PO ₄	Phosphoric acid

Glossary

H ₂ SO ₄	Sulphuric acid
I.D.	Inner (or internal) diameter
In	Indium
LPG	Liquefied petroleum gas
<i>m</i>	<i>meta</i>
MeOH	Methanol
Mg	Magnesium
MgO	Magnesium oxide
MFC	Mass flow controller
MFI	Zeolite ZSM-5
MGC	Mitsubishi gas chemical company
Mn	Manganese
MOR	Zeolite mordenite
MTBE	Methyl- <i>tert</i> -butyl-ether
MTG	Methanol-to-gasoline
MTW	Zeolite ZSM-12
Na	Sodium
Na ₂ O	Sodium oxide
Ni	Nickel
O	Oxygen
<i>o</i>	<i>ortho</i>
O.D.	Outer (or external) diameter
<i>p</i>	<i>para</i>
Pb	Lead
PBR	Packed bed reactor
Pd	Palladium
PI	Pressure indicator
PIC	Pressure indicator and controller
P ₂ O ₅	Phosphorous pentoxide
PPO	Polyphenol oxide
Pt	Platinum
PTAL	<i>p</i> -Tolualdehyde
Si	Silicon
SiO ₂	Silica
SiC	Silicon carbide

Sn	Tin
SS	Stainless steel
TMP	Trimethylphenol
TOS	Time-on-stream
UOP	United Oil Products LLC
V	Symbol in flow sheet denoting a valve
wt	Weight
Z	Symbol denoting a zeolite in diagrams
Z ⁻	Symbol denoting a deprotonated Brønsted acid site of a zeolite
Zn	Zinc

List of Symbols

Symbol	Description	Unit
A	Pre-exponential factor or frequency factor	
A, B, C, D, E	Constants used in heat capacity calculation	J / kmol · K
a	Constant used to trend heat capacity in quadratic format calculations (for linear term)	J / mol · K
A ⁺	Symbol denoting a Lewis Acid site in diagrams	
b	Constant used to trend heat capacity in quadratic format calculations (for square term)	J / mol · K ²
B ⁻	Symbol denoting a Lewis Basic site in diagrams	
c	Constant used to trend heat capacity in quadratic format calculations (for cubic term)	J / mol · K ³
C1, C2, C3...	Constants used in Antoine Equation for vapour pressure calculation	-
C _i	Concentration of species i	gmol / dm ³
C _p (T)	Molar heat capacity	J / mol · K
D _e	Effective diffusivity	dm ² / s
E _A	Activation energy	J / mol
F	Flow rate	ml / h
f _i	GC response factor for species i	-
GHSV	Gas hourly space velocity	ml _{m-cresol} / ml _{active catalyst} · h
ΔG _{f, i} (mol)	Molar Gibbs free energy of formation of species i	J / mol
ΔG _{rxn} (T)	Molar Gibbs free energy of reaction at temperature T	J / mol
ΔH _{f, i} (mol)	Molar heat of formation of species i	J / mol
ΔH _{rxn} (T)	Molar heat of reaction at temperature T	J / mol
ΔH _{ads}	Molar heat of adsorption	J / mol
K _i	Equilibrium constant for reaction i	-
k _n	Specific reaction rate constant	s ⁻¹
LHSV	Liquid hourly space velocity	ml _{m-cresol} / ml _{active catalyst} · h
P	Pressure	bar
P _{atm}	Atmospheric pressure	bar
P _{vap}	Vapour pressure	bar

List of Symbols

PAC_i	Corrected GC peak area of species i	m^2
PA_i	GC peak area of species i	m^2
PAM_i	Mol proportional value of species i	m^2
R	Gas constant ($R = 8.314$)	$J / mol \cdot K$
R	Radius of zeolite crystal	m
S_a	Surface area per unit mass of catalyst	m^2 / g
S_i	Selectivity to species i	mol %
T	Temperature	$^{\circ}C$ (or K)
T_c	Critical temperature	$^{\circ}C$
φ	Diameter	m
Φ_n	Thiele Modulus	-
ν	Stoichiometric coefficient	-
WHSV	Weight hourly space velocity	$g_{m-cresol} / g_{active\ catalyst} \cdot h$
x_i	Mol fraction of species i in vapour or liquid phase	-
X	Conversion	%
X_{eq}	Equilibrium conversion	%
$x_{eq, i}$	Thermodynamic equilibrium molar fraction of species i	-
Y_i	Yield of species i	
Z	Symbol denoting a zeolite in diagrams	
Z^-	Symbol denoting a deprotonated Brønsted acid site of a zeolite	

1. Introduction

Phenol, cresols and xylenols have enormous industrial importance. Cresols and xylenols are important chemicals in the polymers (resins), electronics, pesticides, pharmaceutical, paint and dye industries.

Historically, cresols and xylenols have been obtained from coal tars, coal gasification liquors and spent refinery caustics (the so called “natural” cresols). However for some decades now, the production of cresols and xylenols has been moving away from these traditional sources (due to increasing demand, process restructuring, capacity reductions, plant closures, increasing environmental stipulations etc.) and synthetic processes, including the methylation of phenol and cresols, are being increasingly used.

The selective production of cresols and xylenols is difficult, partly owing to the number of isomers that occur. In addition, many of these isomers have similar boiling points, thus separation via distillation is not always effective and economical. Other possible separation techniques are often complicated and very costly. If processes can be found, whereby individual isomers can be produced at high selectivity, separation costs can be minimised and production may be more economically feasible.

The literature review aims to firstly investigate some of the production methods currently employed for cresols and xylenols and respective industrial companies involved. The economic aspects of cresols and xylenols in the world market are presented. Thermodynamic equilibria and various mechanisms that are reported in literature are discussed for comparison with the results achieved in this work. The properties of the catalysts employed are presented and trends observed by previous researchers are reported for purposes of comparison.

In this work, the synthesis of specific xylene isomers, via methylation of *m*-cresol with methanol over acid catalysts, was investigated, with particular focus on shape-selective zeolites as catalysts and the effect of various reaction parameters. Attention was drawn to the possibility of producing certain isomers, specifically the “slim” isomers, 2,5-xylene and 3,4-xylene, over shape-selective or potentially shape-selective acid zeolite catalysts, namely regular commercial samples of FER, MFI, MOR, MTW and BEA. Results are compared with product distributions obtained over a non shape-selective catalyst, namely, amorphous silica-alumina.

2. Background

2.1 Cresol and xyleneol molecules

Cresols (or methylphenols) are comprised of 7 carbons atoms, 8 hydrogen atoms and 1 oxygen atom (C_7H_8O) and occur as three isomers, as shown in figure 2.1.

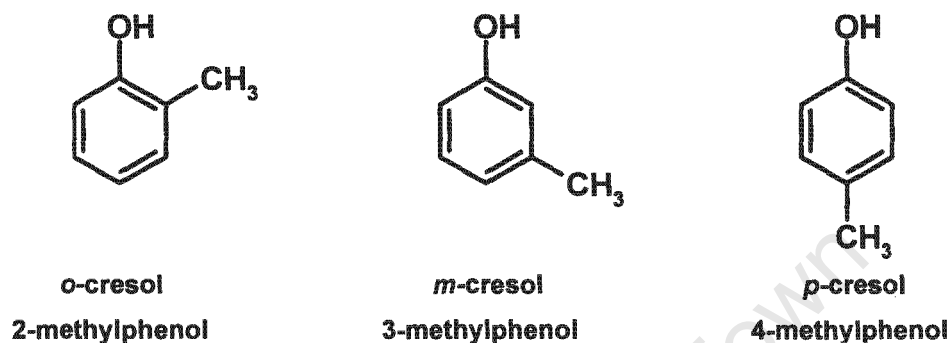


Figure 2-1: The three different cresol isomers

Xylenols (or dimethylphenols) are comprised of 8 carbons atoms, 10 hydrogen atoms and 1 oxygen atom ($C_8H_{10}O$) and occur as six isomers, as shown in figure 2.2.

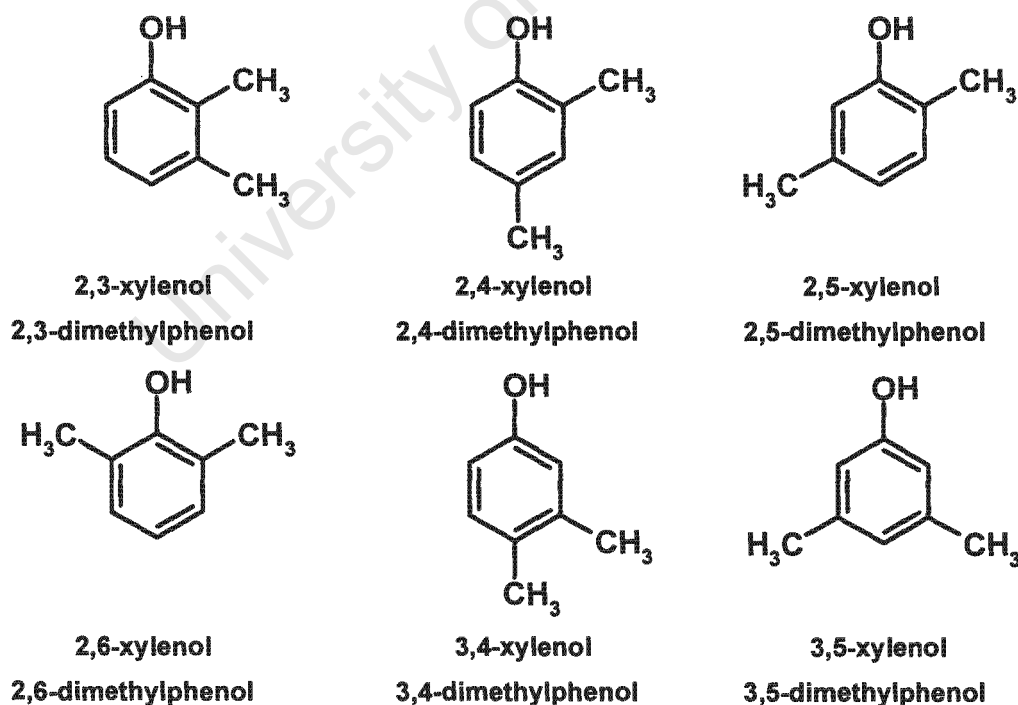


Figure 2-2: The six different xyleneol isomers

Cresols were first discovered in cow's urine in 1851 by Städeler and by 1869 all three isomers had been identified. Since then cresols have been found occurring naturally in

many different sources, including food and beverages such as tea, tobacco and roasted coffee. Commercial cresols were initially extracted from coal tars. Following World War II, they were also extracted from spent refinery caustics. Extraction of cresols from these "natural" sources (coal tars and spent refinery caustics) now accounts for approximately 40 % of annual production of the United States, Europe and Japan. South Africa is also a major producer, extracting 35 000 – 55 000 t / a cresols and xlenols from coal gasification liquors. Since the 1960's, synthetic production of cresols has been increasing and currently accounts for about 60 % of annual requirements of the United States, Europe and Japan (Fiege, 2003).

Xlenols were also discovered in various natural sources, including tea, tobacco and roasted coffee. Commercial xlenols were initially also produced only from coal tars. However, the most demanded isomer, 2,6-xlenol, only occurs naturally in small amounts, even in coal tars, and so it is produced almost completely by synthetic means (Fiege, 2003).

2.2 Physical and chemical properties of cresols and xyenols

At room temperature, pure *o*-cresol and *p*-cresol are crystalline solids, while *m*-cresol forms a viscous oil (Fiege, 2003).

2.2.1 Acidity

Cresols and xyenols are weak acids and dissolve to some extent in water. In basic media such as aqueous sodium hydroxide they form cresolates and xyenolates (water-stable salts) (Fiege, 2003).

2.2.2 Hydroxyl group etherification and esterification

It is possible to etherify the hydroxyl group on a cresol molecule through reaction with various compounds such as alkyl halides, dialkyl sulphates, dialkyl carbonates and toluene sulphonic acid esters, and react it with acyl anhydrides or acyl chlorides to give the corresponding tolyl esters, which are normally referred to as "cresyl" esters. Isocyanates react with the hydroxyl group to form urethanes (Fiege, 2003). Under more severe conditions and in the presence of an acid catalyst, the hydroxyl group can also be etherified with aliphatic alcohols and olefins.

2.2.3 Hydroxyl group substitution

Under severe reaction conditions (over Al_2O_3 at 420°C), the hydroxyl group can be substituted by ammonia, producing the corresponding toluidine isomer. The hydroxyl group on cresols and xyenols can also be replaced with fluorine, chlorine or bromine (these reactions can be carried out with sulphur oxytetrafluoride at 150°C , diphenylphosphine trichloride at 220°C or phosphorus tribromide at 280°C , respectively) (Fiege, 2003).

2.2.4 Reduction and hydrogenation

Reaction with strong reducing agents, such as zinc powder, produces toluene (Fiege, 2003).

Hydrogenation is possible, selectively, of either the hydroxyl group or the aromatic ring.

- Cresol vapour phase hydrogenation at $300 - 400^\circ\text{C}$ and elevated pressure of up to 80 bar over transition metal and aluminium oxide catalysts produces toluene (Fiege, 2003).

- Cresol ring hydrogenation to methylcyclohexanol over palladium, nickel and rhodium catalysts has also been reported (Takagi *et al.*, 1967, Takagi *et al.*, 1968, Zwicky and Gut, 1978, Hichri *et al.*, 1991 and Yanagawa *et al.*, 1985)

2.2.5 Hydrogenative demethylation

Cresols can be demethylated to phenol thermally at temperatures of between 480 – 600°C and with hydrogen partial pressure of 20 – 110 bar (Huibers *et al.*, 1984). Xylenols behave likewise under similar conditions (Fiege, 2003).

2.2.6 Oxidation

Cresols and xylenols are sensitive to oxidation reactions and, depending on the reaction conditions, oxidising agent and position of the methyl group, produce large numbers of different compounds such as cyclic ketones, quinones and hydroquinones. The reaction occurs via a free radical mechanism. The phenol ring is broken by strong oxidising agents (Fiege, 2003).

2.2.7 Condensation reaction

Cresols combine in condensation reactions to form tolyl ethers. This reaction is acid catalysed and produces water as a co-product (Fiege, 2003).

2.2.8 Electrophilic substitution

Cresols and xylenols can undergo electrophilic substitution on the ring. When the electrophile attacks the aromatic nucleus, substitution in the *o*- and *p*- position (from the hydroxyl group) is preferred. Alkylation, nitrosation, halogenation and sulphonation reactions can readily occur (Sykes, 1986). Heating *o*- and *p*-cresol over acid catalysts such as Friedel-Crafts catalysts (e.g. AlCl_3) also produces *m*-cresol, thermally the most stable isomer, via isomerisation. Substitution on the aromatic nucleus competes with substitution on the hydroxyl group (see above) (Fiege, 2003).

2.3 Economic aspects

2.3.1 Global production

2.3.1.1 Cresols

During 1998 approximately 175 000 tons of cresols were produced in the United States, Europe, Japan and South Africa, of which about 105 000 tons (60 %) were produced synthetically and 70 000 tons were extracted as “natural” cresols (from coal tars, coal gasification liquors and spent refinery caustics). About 45 % were either pure *o*-cresol or pure *p*-cresol, with the remained comprising mainly isomer mixtures (Fiege, 2003).

2.3.1.2 Xylenols

In 1998 the total xylenols output in the United States, Western Europe and Japan was approximately 165 000 tons. Of this, 2,6-xyleneol comprised approximately 125 000 tons, with xyleneol mixtures encompassing 30 000 – 40 000 tons and other individual pure isomers (mainly 2,4-, 2,5- and 3,5-xyleneol) making up about 10 000 tons.

Xyleneol mixtures were mainly obtained from coal tars and spent refinery caustics. In the United States, Europe and Japan xylenols were also produced via synthetic routes, in particular the 2,6-xyleneol isomer (Fiege, 2003).

2.3.2 Prices

Although the prices of phenols, cresols and xylenols vary with quality, supply and demand, some approximate prices paid in the period 1992 – 2004 are shown in table 2-1. It is apparent that where isomer mixtures are separated into pure compounds, the value of the product increases. However, the value of pure *o*-cresol is much lower than that of pure *m*- or *p*-cresol. This is due to the cost of separation. While *o*-cresol can easily be distilled off a mixture of cresols, due to the similarities in their boiling points, *m*- and *p*-cresol cannot be separated economically via distillation. Of the three isomers, *o*-cresol boils at 191.00°C, while *m*- and *p*-cresol boil at 202.23°C and 201.94°C respectively (see table 2-9) (Fiege, 2003).

The same holds for some of the xyleneol isomers as they are also difficult to separate. Thus, if xyleneol isomers can be produced at high selectivity the complexities and costs of separation will be minimised and the production costs will be reduced. One of the sources referred to in table 2-1 indicated that some pure xylenols sell for up to US\$ 10 000 per ton. This was a substantial increase in value compared to cresols as the potential raw material.

Table 2-1: Approximate prices of phenol, cresols and xlenols

	1992*	1996**	1997***	2004****
Product	US\$ / ton			
Phenol	700	900	900	700 – 800
<i>o</i> -Cresol	1390		1511	1200 – 1400
<i>m</i> -Cresol	3760		2556	2400 – 2700
<i>p</i> -Cresol	2790	1 500 – 3 000	3044	1500 – 2200
<i>m</i> - / <i>p</i> -Cresol mixtures	–		2089	1100 – 1300
Xlenols	–	Individual isomers up to 10 000	–	Normally sold as mixtures 1800 – 2800

*Lorence et al. (1992) from Böhringer (2002)

**EPA (1996) from Böhringer (2002)

***EPA (1997) from Böhringer (2002)

****Goolam (2004)

2.4 Industrial manufacture

Cresols and xlenols are currently produced by a number of different industrial processes. Following are a brief description of some of the major production methods that are being, or have been used.

2.4.1 Isolation of natural cresols and xlenols

Cresols and xlenols have conventionally been produced and still are produced as by-products from tars and liquors obtained in the coking and gasification of coal and from spent refinery caustics obtained in crude oil refining.

However, the sources of “natural” cresols and xlenols have been declining continuously over the past few decades with the decreasing availability of coal tars and spent refinery caustics due to sharper environmental regulations and increasing environmental costs (especially in the United States and Europe) and restructurings, capacity reductions and plant closures of some of the major industrial processes producing “natural” cresols and xlenols (Fiege, 2003).

2.4.1.1 Isolation from coal tars

Extraction of cresols and xlenols from coke oven tars has been a traditional source, yielding around 30 000 – 40 000 t/a, with products obtained from high-temperature coke-oven tar, produced in the horizontal chamber coking of bituminous coal. The process takes place at around 900 – 1300°C. Typical yields of phenolic products are as shown in table 2-2.

Table 2-2: Yields of phenolic products from coal coking tars (Elliot, 1981)

Product	Yield (wt %)
Phenol	0.4 – 0.6
Cresols	0.8 – 1.0
Xlenols	0.2 – 0.5

Phenol, cresols and xlenols are also extracted from low temperature coal tars, where the content of C₆ – C₈ phenols is typically 10 times higher, although in the last decade these tars have become much less abundant (Fiege, 2003).

Often, in “natural” mixtures, *m*- and *p*-cresol (boiling points of 202.23°C and 201.94°C respectively) are lumped together with 2,6-xyleneol (boiling point of 201.03°C) and sometimes 2-ethylphenol (boiling point of 204.5°C) because the similarities in boiling points make separation very difficult (see table 2-9 for boiling point comparison).

In high temperature coal tars, the most common xyleneol isomer is 3,5-xyleneol. A typical xyleneol isomer distribution in high temperature bituminous coal tar is shown in table 2-3.

Table 2-3: Average distribution of xyleneol isomers in high temperature bituminous coal tars (Fiege, 2003)

Product	Distribution (%)
2,3-xyleneol	14
2,4-xyleneol	28
2,5-xyleneol	13
2,6-xyleneol	7
3,4-xyleneol	6
3,5-xyleneol	32

Sasol, in South Africa, currently provides the largest source of natural cresols (35 000 – 55 000 t/a) from the gasification of bituminous coal in Lurgi gasifiers (Fiege, 2003). The Dakota Gasification Co in the United States gasifies lignite, producing C₆ – C₈ phenols as co-products (Baker et al., 1990). The distribution of the phenolic products from gasifying lignite in Lurgi gasifiers is given in table 2-4 (Fiege, 2003).

Table 2-4: Distribution of phenols obtained in Lurgi gasifier tar from lignite at Dakota Gasification Co (Fiege, 2003)

Product	Distribution (wt%)
Phenol	4
<i>o</i> -Cresol	5
<i>m</i> -Cresol	8
<i>p</i> -Cresol	7
Xylenols	24
Higher phenols	52

2.4.1.2 Recovery from spent refinery caustics

Cresols and xlenols may be obtained from the naphtha fractions produced in catalytic and thermal cracking of heavy crude oil fractions, especially from Fluidised Catalytic Cracking (FCC). On average, the cresols and xlenols content of the cracking naphtha is around 0.1 %. These naphtha fractions also contain various acid sulphur compounds (such as thiols) that are removed in a "sweetening" process, where the naphtha is scrubbed with solution of caustic. The acidic phenol, cresols and xlenols are also removed in the "sweetening" process and appear in the spent caustic. $C_6 - C_8$ phenols contribute between 20 – 25 % of the total organic content of the spent caustics and sulphur compounds contribute 10 – 15 %. Table 2-5 shows the distribution in the phenol mixtures obtained in this way (Fiege, 2003).

Table 2-5: Distribution of phenols obtained via extraction of catalytic cracker naphtha by alkaline solution (Fiege, 2003)

Product	Distribution (wt %)
Phenol	20
<i>o</i> -Cresol	18
<i>m</i> -Cresol	22
<i>p</i> -Cresol	9
Xlenols and ethylphenols	28
Higher phenols	3*

**Note that this low percentage is due to the high boiling points of these compounds, being above the boiling range of naphtha.*

When extracted from spent refinery caustics, the most prevalent xlenol isomer is usually 2,4-xlenol followed by 2,5-xlenol. In contrast to xlenols from coal tars, the percentage of 3,5-xlenol is relatively low (Fiege, 2003).

The recovery of cresylics from spent refinery caustics has been confined to the United States, as different refinery techniques (such as de-sulphurisation through hydrotreating) are being employed in other countries. In Germany, for example, the production of cresol-containing spent caustics is too low to justify economical processing. However, due to increased competition from synthetic *o*-cresol producers, increasing environmental restrictions that are forcing the phasing out of the sweetening process and therefore an

overall lack of raw materials, many producers of “natural” phenolics in the United States have closed down respective operations, leaving Merichem as the only remaining processor of spent refinery caustics. In 1996 Merichem’s “cresylics” capacity was about 55 000 t/a (including cresylics from other sources) (Fiege, 2003).

As mentioned above, in the United States, the production of cresylics from spent refinery caustics is declining. This too, is mainly due to the conversion of de-sulphurisation processes from sweetening to hydro-treating or the UOP Merox process so that, increasingly, the low amounts of cresylics are left in the gasoline fraction. Some refiners indeed desire to keep the phenolics within the gasoline fraction as the cost of extraction is high and phenolics boost the overall octane number. It has been suggested that phenolics cause harm to the engine cylinder during the combustion process through deposition of gums in the combustion chamber, however recent research has proved that this is not the case (UOP, 2004). So the decline in phenolics from refineries will continue.

2.4.2 Synthetic production of cresols and xyenols

As mentioned above, with the increasing demand of cresols and xylenols, production through isolation from coal tars and refinery caustics has become unable to supply demand. Thus, processes have been developed to manufacture these products via synthetic routes.

2.4.2.1 Methylation of phenol and cresol

The methylation of phenol (and sometimes cresol) in the presence of catalysts is being used increasingly in the production of cresols (especially *o*-cresol) and xylenols (especially 2,6-xyenol, which is produced almost entirely via this method). For this reaction, refer to figure 2-3.

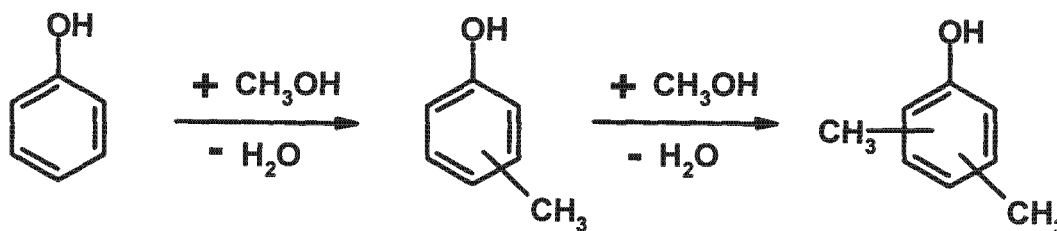


Figure 2-3: Phenol methylation with methanol to cresols and xylenols

However, there are certain problems associated with this process. Firstly, phenol is a relatively expensive material. Secondly, the separation of the cresol / xylenol mixtures

produced is difficult and often very expensive, due to the similarity of boiling points (see section 2.4.3 and table 2-9).

However, there is only one reaction step in phenol alkylation to cresols and xylenols and the reaction may be carried out with different selectivity over basic, acid and amphoteric catalysts in either vapour or liquid phase, as discussed below.

2.4.2.1.1 Basic catalysts (Fe / VO_x, MgO etc.)

Literature reports the use of many different basic metal oxide catalysts that are used industrially. The basic metal oxide catalysts tend to be highly *ortho* selective, with >99.5 % selectivity being achieved in some cases. Conversion is often kept below 60 % to prevent secondary reactions (Fiege, 2003).

The product mixture is fractionated into phenol ether, phenol, cresol (99.5 % *o*-cresol) and xylene (>99.5 % 2,6-xylene) in a series of distillation columns. The residue (which can contain small amounts of other xylene isomers and some trimethylphenols) is usually burnt as fuel. The ratio of *o*-cresol to 2,6-xylene can be controlled by altering the methanol : phenol feed ratio. *o*-Cresol and 2,6-xylene selectivity of 90 – 98 % (on converted phenol) are achieved over extended time-on-stream. Increasing the severity of the reaction can increase the amounts of *m*- and *p*-cresol formed (Fiege, 2003).

These vapour phase catalysts typically operate at low pressure. In general, basic metal oxide catalysts are operated at higher temperatures (~320 – 400°C) than acidic metal oxide catalysts (~300°C), see tables 2-6 to 2-8. A more detailed list of operating temperatures is available in literature (Fiege, 2003).

Table 2-6: Typical operating temperature of basic catalysts, as used in phenol methylation to cresols and xylenols (Fiege, 2003)

Catalyst	Operating Temperature (°C)
Iron-/ Vanadium Oxide	320 – 340
Magnesium Oxide	420 – 460
Manganese Oxide	380 – 400
Chromium Oxide	380 – 400
Iron Oxide	320 – 350
Vanadium Oxide	320 – 350

Small amounts of various metal oxides (e.g. Ce, Cr, Mn, Co, Ni, Zn, Al, Ga, In, Si, Ge, Sn, Pb, Bi, Mg, Na) may be added to further promote the reaction. These catalysts show excellent *ortho* selectivity.

Phenol methylation over iron based catalysts is accompanied by methanol decomposition to H₂ and CO (Fiege, 2003). However, this is desired by some manufacturers to balance the exothermic phenol alkylation with this endothermic reaction (Böhringer, 2004).

'O' alkylation is catalysed by alkali metal-loaded catalysts, where the reactivity of the catalyst increases with basicity (Lee *et al.*, 1998 and Velu *et al.*, 1996).

2.4.2.1.2 Amphoteric (Al₂O₃)

Under mild conditions, in particular at low temperature (300 – 350°C), γ -alumina is quite *o*-selective, acting as a base. Below 300°C increasing amounts of anisoles are formed. At higher temperatures γ -alumina becomes *o*- and *p*- selective (Fiege, 2003). Typical phenol methylation reaction temperatures over amphoteric catalysts are shown in table 2-7.

Table 2-7: Typical operating temperature of amphoteric catalysts, as used in phenol methylation to cresols and xylenols to produce an *ortho* selective product (Fiege, 2003)

Catalyst	Temperature (°C)
Alumina	300 – 320
Aluminium Phosphates	300 – 350
Aluminium Methylate	350 – 400

Reaction over γ -Al₂O₃ at 300 - 320°C has been reported for methanol : phenol feed ratio of 0.5 at liquid hourly space velocity of 1 h⁻¹. At these conditions, *o*-cresol, 2,6-xyleneol, and *m*- / *p*-cresol mixture are formed in molar ratio of 82 : 17: 1, with total selectivity of 97 % and a phenol conversion of 33 %. Increasing the methanol : phenol feed ratio or recycling *o*-cresol shifts the product distribution towards 2,6-xyleneol. Below 300°C increasing amounts of anisole are formed on γ -Al₂O₃. At this low temperature anisole is not sufficiently converted to *o*-cresol. With increasing residence time and reaction temperature phenol conversion increases, but *ortho* selectivity falls (Fiege, 2003).

2.4.2.1.3 Acid catalysts (silica-alumina, Friedel-Crafts catalysts, zeolites)

At high temperatures acid catalysts have shown high *o*- and *p*- selectivity, refer to table 2-8 (Fiege, 2003).

High *ortho* and *para* selectivities are achieved over these catalysts, but total phenol conversion is kept below 60 % to prevent secondary and tertiary alkylation (Fiege, 2003).

Table 2-8: Typical operating temperature of acid catalysts, as used in phenol methylation to cresol and xylenols (Fiege, 2003)

Catalyst	Temperature (°C)
γ – Aluminium Oxide (gas phase)	300 – 320
γ – Aluminium Oxide (liquid phase)	300 – 400
Zeolite H-KY	250 – 300
Phosphoric acid	250 – 300
Zinc – Halide	250 – 300
Hydrogen - Halide	250 – 300

2.4.2.2 Alkali fusion of toluene sulphonates and xylene sulphonates

Alkali fusion of toluene sulphonates, the primary route to manufacturing *p*-cresol at high selectivity, comprises a four step process. Firstly toluene is sulphonated with concentrated sulphuric acid to toluene sulphonic acids. The product is further reacted with sodium sulphite to sodium tolyl sulphonate and fused with excess sodium hydroxide to sodium cresolates and sodium sulphite. Hydrolysing with water produces a crude cresol product which is high in the *p*-isomer (Fiege, 2003). It is the sulphonation step in this reaction that is highly *para* selective. In comparison, substitution in the *ortho* position is suppressed by steric hindrance and substitution in the *meta* position is also suppressed as the *meta* position is less reactive (Sykes, 1986).

The crude cresol product is separated into phenol, *o*-cresol, *m*- / *p*-cresol mixture and other products through fractional distillation. Typical raw cresol product mixtures comprise of 6–12 % *o*-cresol, 6–12 % *m*-cresol and 80–85 % *p*-cresol. After removing *o*-cresol (through distillation), a *p*-cresol fraction with purity of ca. 90 % can be obtained. This can be further improved to 99 % through fractional crystallization. Manipulating the process further can produce *p*-cresol at increased purity.

When xylene is used as the reactant, xyenol isomers are produced. Sulphonation of *m*-xylene at 150°C leads to formation of 2,4-xylenol at yields of up to 79 %. When the reaction is carried out at 220°C the more thermodynamically stable isomer, 3,5-xylenol is produced and by employing slightly different reaction procedures and techniques 3,5-

40. High quality acetone is produced. Difficult separation procedures are required to further separate and purify the *m*- / *p*-cresol product mixture (Fiege, 2003).

Mitsubishi Gas Chemical Company, in Japan, produces 3,5-xyleneol via oxidation of 3,5-dimethylcumene to 3,5-dimethylcumene hydroperoxide, which is then cleaved. This reaction is more expensive than the comparative cumene-cresol reaction as the added methyl group leads to more side reactions (Fiege, 2003).

2.4.2.5 Transmethylation and isomerisation

Adding phenol to methylphenol residues or to xylenols in the presence of alkylation catalysts produces mainly *o*-cresol, but also *m*- and *p*-cresol. This reaction may take place in either liquid or gas phase at high temperatures of 400 – 500 °C. Typical catalysts used in this reaction are aluminium oxide, chromium oxide – aluminium oxide and magnesium oxide – tungsten oxide. The Chiyoda Chemical Engineering Construction Company has developed an isomerisation–transalkylation process with phenol on silica-alumina catalyst. *m*-Cresol or *p*-cresol can be separated by passing the mixture through a modified Y zeolite adsorption unit (see section 2.5.3), and recycling the unwanted product (Fiege, 2003).

Not many zeolites are used in transmethylation of phenolics as there is not sufficient space inside the pore chamber for bimolecular reactions to occur (Fiege, 2003).

Processes for isomerising *o*-cresol to *m*- / *p*-cresol have been investigated, although many attempts have been unsuccessful due to resinification and disproportionation to phenols and dimethylphenols (Fiege, 2003).

However, isomerisation without substantial disproportionation is possible on shape selective zeolites of the ZSM group at temperatures of around 400 °C with *o*-cresol conversions of 40 – 50 %, *m*- / *p*-cresol selectivities of 90 % and a *m*- : *p*- ratio in the product of 7 : 3 (Fiege, 2003) i.e. the composition of the cresols is close to thermodynamic equilibrium values (Imbert *et al.*, 2000, Fritsch *et al.*, 2003).

2.4.2.6 Demethanisation of isophorone

This method is used primarily to produce 3,5-xyleneol, which is not normally a product of the phenol or cresol methylation processes and is only isolated in limited amounts from the natural xyleneol mixtures. This process, used by Inspec Fine Chemical in the UK, involves the demethanisation of isophorone according to a process developed by Shell. Isophorone is produced via the cyclic trimerisation of acetone over basic catalysts in an aldol condensation type reaction. Homogeneous catalytic processing is possible here with 1 wt % methyl iodide added to the isophorone. The reaction is carried out in vapour

phase, at a temperature of 600 °C and extremely low pressure of 0.001 bar. Over a cobalt-molybdenum-potassium oxide- γ -aluminium oxide catalyst, a 3,5-xyleneol yield of about 70 % is achieved, although a variety of by-products are also formed (Fiege, 2003).

2.4.2.7 Other routes

The following are some other processes that have been developed on small scales but have not been commercialised.

2.4.2.7.1 Gulf oxychlorination

The Gulf Research Co. has developed a process where toluene is catalytically oxychlorinated with hydrochloric acid and oxygen at 100 °C. At a toluene conversion of 80 % and a product with *o*- : *p*-chlorotoluene ratio of 2 : 1 and chlorotoluene selectivity of >95 % is achieved. This is then hydrolyzed in the vapour phase at 400 – 450 °C over a catalyst, such as lanthanum phosphate, to cresol, with large amounts of *o*-cresol obtained and some *p*- and *m*-cresol. Xylenols can also be produced via this method. However, commercial application of this process has not taken place (Fiege, 2003).

2.4.2.7.2 Oxidative decarboxylation of methylbenzoic and dimethylbenzoic acids

In this process, methylbenzoic acids are decarboxylated to cresols when an air / steam mixture is passed through their melt. Methylbenzoic acids can be obtained from oxidation of xylene, although this is an expensive raw material (Fiege, 2003).

This process is quite complicated and not very selective. However, the process could be used in the manufacture of *m*-cresol as only *m*-cresol is formed from both *p*- and *o*-methylbenzoic acid. Xylenols are produced through oxidative decarboxylation of dimethylbenzoic acids (Fiege, 2003).

2.4.2.7.3 Baeyer-Villiger oxidation of *p*- or *o*-methylbenzaldehyde

In this process, hydrogen peroxide reacts with excess formic acid to produce performic acid. Performic acid oxidizes *p*-methylbenzaldehyde to *p*-tolyl formate, which is then hydrolysed with water to produce *p*-cresol at yields > 80 % and formic acid. *p*-Methylbenzaldehyde can be produced by reacting toluene and carbon monoxide in the MGC PTAL process, as developed by Mitsubishi (Fiege, 2003).

2.4.2.7.4 Toluene hydroxylation

Rhône-Poulenc report that cresols from toluene hydroxylation have been obtained with 85 % hydrogen peroxide in the presence of a large amount of trifluoromethanesulphonic

acid and a small amount of phosphoric acid. An *o*- / *p*-cresol ratio of 2 : 1 was obtained with 80 % yield (on basis hydrogen peroxide) at a toluene conversion of 10.6 % (Fiege, 2003).

Using titanium modified zeolites, such as TS-1 and hydrogen peroxide, a hydroxylation process was developed by Enichem, Italy. An *o*-, *m*-, and *p*-cresol mixture of ratio 14 : 11 : 75 was obtained at 40 % yield, based on hydrogen peroxide (Fiege, 2003).

It was also found that hydroxylation of toluene with specific micro-organisms gives regioselectively *p*-cresol (Fiege, 2003).

Xylenols can also be produced through xylene hydroxylation (Fiege, 2003).

However, processes involving hydroxylation of the aromatic nucleus of aromatic hydrocarbons have been unsatisfactory, as cresols must be isolated from very dilute solutions, and large amounts of unreacted starting materials and auxiliaries must be recycled with as little waste as possible (Fiege, 2003).

2.4.3 Separation

Separation of cresol and xlenol isomers presents a large challenge as *m*-cresol, *p*-cresol and 2,6-xlenol have very close boiling points, and thus cannot be separated through distillation (table 2-9). The problem is exacerbated when ethylphenols are present too, such as with natural phenolic mixtures, since *o*-ethylphenol also boils very close. Instead, other, more complicated and usually more expensive methods must be used. Thus the advantage of producing one of the isomers with high selectivity can be seen as the costs of separation will be dramatically reduced.

Table 2-9: Melting and boiling points for cresol, xyleneol and ethylphenol isomers at 1.013 bar (Fiege, 2003)

Component	Melting Point (°C)	Boiling Point (°C)
<i>o</i> -cresol	30.99	191.00
<i>m</i> -cresol	12.22	202.23
<i>p</i> -cresol	34.69	201.94
2,3-xyleneol	72.57	216.87
2,4-xyleneol	24.54	210.93
2,5-xyleneol	74.85	211.13
2,6-xyleneol	45.62	201.03
3,4-xyleneol	65.11	226.95
3,5-xyleneol	63.27	221.69
<i>o</i> -ethylphenol	-3.3 -28.0*	204.5
<i>m</i> -ethylphenol	-4.5	218.4
<i>p</i> -ethylphenol	45.1	218.0

*metastable

Some of the separation methods that are used in industry to separate mixtures of phenolic products are described below.

2.4.3.1 Distillation

Distillation is often the first choice of the separation methods, because it is much less complicated than other separation processes and because the operating costs are generally lower when compared to other separation procedures. However, distillation cannot be used to totally separate mixtures of cresols and xyleneols, since some compounds have close boiling points, so more expensive and complicated techniques have to be used.

Table 2-9 shows the different boiling points for cresol, xyleneol and ethylphenol isomers at 1.013 bar.

Due to its much different boiling point, *o*-cresol can be separated out of a cresol mixture via distillation, but *m*-cresol and *p*-cresol cannot be separated economically via distillation

as their normal boiling points are too close (202.23°C and 201.94°C, respectively). To make things even more complicated, the normal boiling point of 2,6-xyleneol and *o*-ethylphenol are 201.03°C and 204.5°C, respectively. The normal boiling points of 2,4- and 2,5-xyleneol (210.93°C and 211.13°C, respectively) and of 3,4- and 3,5-xyleneol (226.95°C and 221.69°C, respectively) are also close together, making separation difficult.

2.4.3.2 Crystallization

At atmospheric pressure it is possible to separate *p*-cresol from *m*- / *p*-cresol mixtures containing more than 58 % *p*-cresol, and *m*-cresol from *m*- / *p*-cresol mixtures containing more than 89 % *m*-cresol through fractional crystallization. Within this range the *m*- and *p*-cresol form a eutectic mixture (2 : 1 *m*- : *p*-cresol ratio) and thus separation through crystallization is not possible (Fiege, 2003).

2.4.3.3 Adsorption

Alkali metal-modified or alkaline earth metal-modified zeolites of the types X, A, L or ZSM-5, also titanium oxide are used to adsorb *p*-cresol out of *m*- / *p*-cresol mixtures.

Modified faujasite zeolites (X and Y) are used to separate out 3,5-xyleneol from close boiling 3,4- / 3,5-xyleneol mixtures, where 3,4-xyleneol is adsorbed, leaving 3,5-xyleneol unadsorbed.

SrX zeolites are used to adsorb 2,4-xyleneol out of close boiling mixtures also containing 2,5-xyleneol and *m*-ethylphenol.

Cresols are more readily adsorbed on zeolites of the type K–Ba–X than 2,6-xyleneol, thus 2,6-xyleneol can be separated from *p*- and *m*-cresol through this method (Fiege, 2003).

2.4.3.4 Electrophilic substitution

Industrially *m*- and *p*-cresol are separated via their di-*tert*-butyl derivatives. In this process 1 mol of *m*- / *p*-cresol mixture is reacted with 2 mols of isobutene in the presence of acidic catalysts (normally sulphuric acid at 100 – 150°C), producing mainly 2,6-di-*tert*-butyl-*p*-cresol (with boiling point of 147°C at 2.67 kPa) and 2,6-di-*tert*-butyl-*m*-cresol (with boiling point of 167°C at 2.67 kPa). Once the catalyst has been deactivated these compounds can be separated easily through distillation. By-products from this process include monobutylated cresols (boiling point of 124 – 129°C at 2.67 kPa), which are returned to the alkylation reactor, and dimers, trimers and possibly tetramers of isobutene, which are also removed. *m*-Cresol and *p*-cresol and isobutene are recovered from the system through dealkylation of the di-*tert*-butylcresols at ca. 200°C in the presence of acidic

catalysts (e.g. sulphuric acid). The individual cresol isomers can be purified further through distillation. Apart from producing the pure *m*- and *p*-cresol isomers, this process is attractive in that 2,6-di-*tert*-butyl-*p*-cresol (BHT, a widely used antioxidant) is produced simultaneously (Larkin, 1943 and Fiege, 2003).

2.4.3.5 Other methods of separation

Other separation techniques, including separation via azeotropic rectification, via counter current extraction and via addition of other compounds and separation via ester or salt formation are employed (Fiege, 2003).

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2.5 Uses

2.5.1 Cresols

In Europe, most of the *o*-cresol is chlorinated and used in the manufacture of herbicides. Smaller amounts are nitrated and used in both herbicide manufacture and as a polymerization inhibitor in the production and distillation of styrene (Fiege, 2003). In Japan, particularly, very pure *o*-cresol is being increasingly used in the production of epoxy resins, which are used in sealing integrated circuits. Common quality *o*-cresol is used to modify traditional phenol-formaldehyde resins (Fiege, 2003).

o-Cresol is also used as a dye intermediate, as a solvent, in the synthesis of coumarin, in the production of fragrances and antiseptics and in the production of antioxidants and pharmaceuticals (Fiege, 2003). Alkylation of *o*-cresol with propene gives 3-isopropyl-6-methylphenol (carvacrol). Carvacrol is used as an antiseptic and in fragrances (ATRSDR, 2005).

m-Cresol, either pure or in mixture with *p*-cresol, is used in pesticide manufacture. Pure *m*-cresol is used in production of vitamin E, fragrances, flavour substances and antioxidants. Pure *m*-cresol is also used in the production of photoresist compositions and thermal recording material, as well as in the manufacture of explosives (Fiege, 2003).

p-Cresol, pure or mixed with *m*-cresol is used in manufacture of antioxidants (particularly 2,6-di-*tert*-butyl-*p*-cresol or BHT), in the production of styrene and in the fragrance industry. Pure *p*-cresol is used in the flavouring and dye industries and in the manufacture of films, coatings and UV light absorbers (Fiege, 2003).

An important application of cresol mixtures is in the production of phenolic resins through condensation with formaldehyde. Mixtures of *p*- and *m*-cresol (free of *o*-cresol) are used to produce phosphoric acid esters, used as flame retardants. They are also used as disinfectants, wool preservatives, synthetic tanning agents, for ore flotation, fibre treatment, extracting solvents and in the paint and textile industry (Fiege, 2003).

2.5.2 Xylenols

Xylenols mixtures are used as solvents, disinfectants, textile auxiliaries and in ore flotation. Mixtures, particularly rich in 3,5-xylenol, are used in xylenols-formaldehyde resins. Major uses of pure xylenols are the following (Fiege, 2003):

- 2,3-Xylenol is only really used in pesticide manufacture.

- Mixtures of 2,4- and 2,5-xyleneol are used as raw materials for synthesising anti-oxidants, especially those for gasoline and rubber.
- 2,5-Xyleneol is used in pharmaceuticals manufacture.
- 2,6-Xyleneol is mainly used to produce poly phenylene oxide (PPO) resins (characteristic for their high impact resistance, thermal stability, fire resistance and dimensional stability) and oxidised to 2,6-xyleneol dimer used to produce epoxy resins for encapsulating semi-conductors. 2,6-Xyleneol is also used in pesticide manufacture, the production of pharmaceuticals and the manufacture of disinfectants.
- 3,4-Xyleneol is used in pesticide manufacture.
- 3,5-Xyleneol is used in pesticide manufacture and in the production of vitamin E. It is also used in the production of disinfectants and industrial preservatives.
- Each of the pure xyleneol isomers (in smaller amounts) is also used in the synthesis of dyes and fragrances.

2.6 Thermodynamic and kinetic aspects of the cresol methylation process

2.6.1 Thermodynamics

2.6.1.1 Cresol methylation

The thermodynamic limits of a reaction are important in defining the absolute limits of that reaction. Given enough time and within existing reaction pathways, every reaction will progress towards equilibrium distribution within the product mixture.

Table 2-10: Calculated $[-\Delta G_{\text{rxn}} / R \cdot T]$ values and conversion at 25°C for *m*-cresol methylation to each of the xylene isomers (1 : 1 molar feed ratio) and for methanol to dimethylether in ideal gas phase (see appendix 1, thermodynamic data from Daubert *et al.*, 1999)

Reaction producing xylene isomer or dimethylether	$-\frac{\Delta G_{\text{rxn}}^{25^\circ\text{C}}}{R \cdot T}$	Conversion (%) (at 25°C)
<i>m</i> -cresol + methanol $\rightleftharpoons$ 2,3-xylene + water	24.0	100
<i>m</i> -cresol + methanol $\rightleftharpoons$ 2,4-xylene + water	27.7	100
<i>m</i> -cresol + methanol $\rightleftharpoons$ 2,5-xylene + water	26.5	100
<i>m</i> -cresol + methanol $\rightleftharpoons$ 2,6-xylene + water	26.3	100
<i>m</i> -cresol + methanol $\rightleftharpoons$ 3,4-xylene + water	24.4	100
<i>m</i> -cresol + methanol $\rightleftharpoons$ 3,5-xylene + water	26.4	100
2 methanol $\rightleftharpoons$ dimethylether + water	6.8	98

Table 2-10 shows the $-\Delta G_{\text{rxn}} / R \cdot T$ values for *m*-cresol methylation to xylene and water at 25°C. In general, when $-\Delta G_{\text{rxn}} / R \cdot T \gg 1$ the reaction essentially proceeds to completion, as shown by the conversions, which indicate that the reaction (at 25°C) proceeds to completion. The reaction forming 2,4-xylene has the largest $-\Delta G_{\text{rxn}} / R \cdot T$, so this reaction will proceed closest to completion.

The $-\Delta G_{\text{rxn}} / R \cdot T$ for the reaction where two moles of methanol form dimethylether and water is also given in table 2-10. It can be seen that the $-\Delta G_{\text{rxn}} / R \cdot T$ for this reaction is much lower than for the xylene forming reactions (but still > 1), so this reaction can occur to a large extent as well.

Figure 2-4 shows the thermodynamic conversion for *m*-cresol methylation with methanol forming e.g. 2,5-xylene and water over temperature range of 0°C to 500°C. It can be seen

that the conversion over this range of temperatures is very close to 100 %. This trend and order of magnitude is similar for all the reactions forming xylenol isomers via the methylation of *m*-cresol. Note that the number of moles doesn't change, so there is no pressure effect.

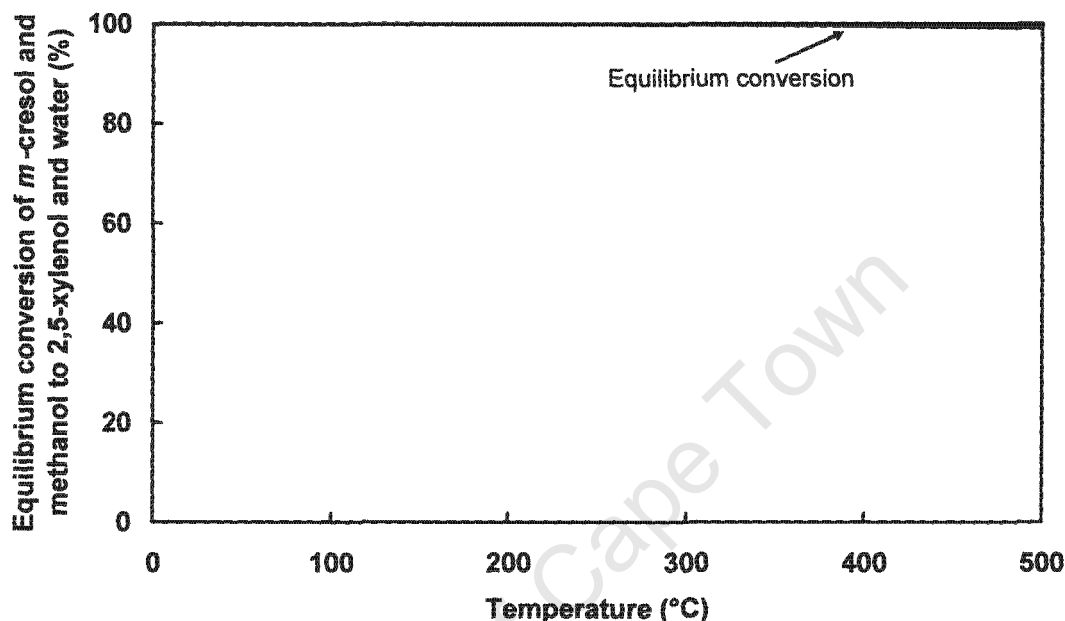


Figure 2-4: Calculated thermodynamic equilibrium conversion of *m*-cresol and methanol (1 : 1 molar feed ratio) to 2,5-xylenol and water as a function of temperature, in ideal gas phase (see appendix 1, thermodynamic data from Daubert *et al.*, 1999)

Figure 2-5 shows the conversion of methanol to dimethylether and water for a temperature range of 0°C to 500°C. It can be seen that if the reaction occurred at 0°C, the conversion of methanol would be near 100 %. When the reaction occurs at elevated temperatures, the conversion of methanol and formation of pre-equilibrium of methanol and dimethylether will still be high. In commercial production of dimethylether from methanol the feed is normally heated to approximately 250°C prior to entry to the reactor. The reaction is carried out over an amorphous alumina catalyst with 10.2 % silica and being slightly exothermic, heats the product mixture to approximately 365°C. The reaction is carried out at approximately 15 bar. The reported equilibrium conversion under these conditions is 92 % (Department of Chemical Engineering, 2005). Thus the thermodynamic equilibrium values calculated here compare well with those reported in industry.

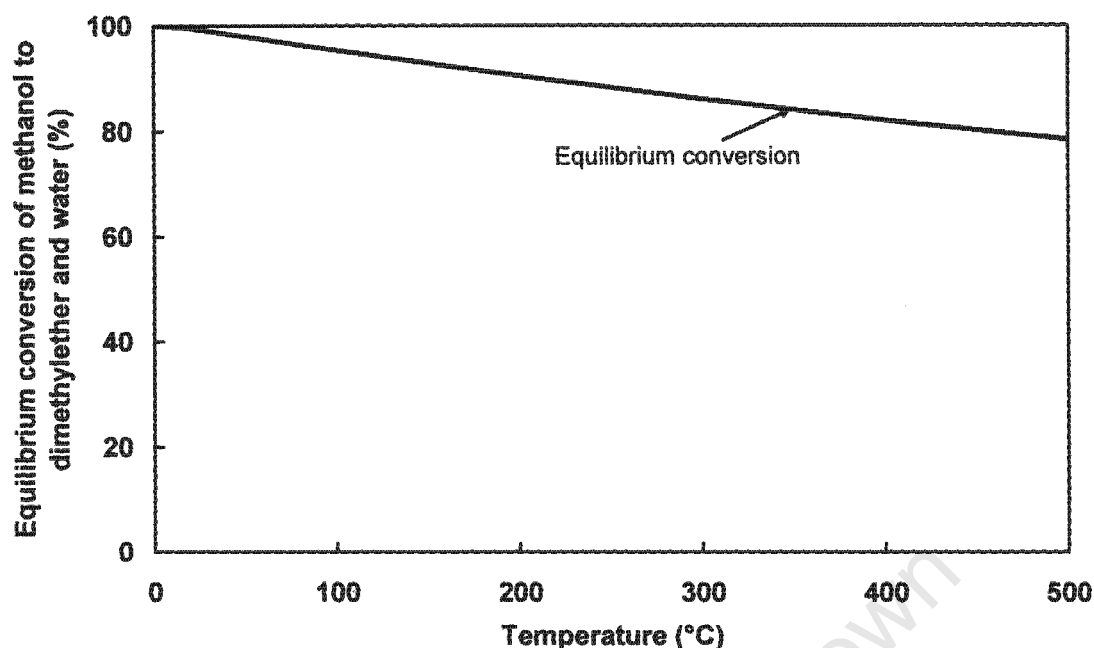


Figure 2-5: Calculated thermodynamic equilibrium conversion of methanol to dimethylether and water as a function of temperature in ideal gas phase (see appendix 1, thermodynamic data from Daubert *et al.*, 1999)

Figure 2-6 shows the distribution of the xylene isomers within the ideal gas phase thermodynamic equilibrium mixture as a function of temperature for temperatures ranging from 100°C to 500°C (as calculated from data taken from Daubert *et al.*, 1999, see appendix 1). Isomer 2,4-xylene is most prevalent. However, with increasing temperature the proportion of 2,4-xylene within the equilibrium mixture falls a little as proportions of all the other isomers increase.

Figure 2-7 shows the 2,5- : 2,3-xylene, 2,5- : 3,4-xylene and 3,4- : 2,3-xylene ratios (the major, primarily formed xylene isomers from *m*-cresol methylation) within gas phase thermodynamic equilibrium of xylene isomers (as calculated from data taken from Daubert *et al.*, 1999, see appendix 1). In the first two cases that ratio falls as temperature increases. At a temperature of 350°C the calculated ratio of 2,5- : 2,3-xylene is 5.0 and the calculated ratio of 2,5- : 3,4-xylene is 2.9.

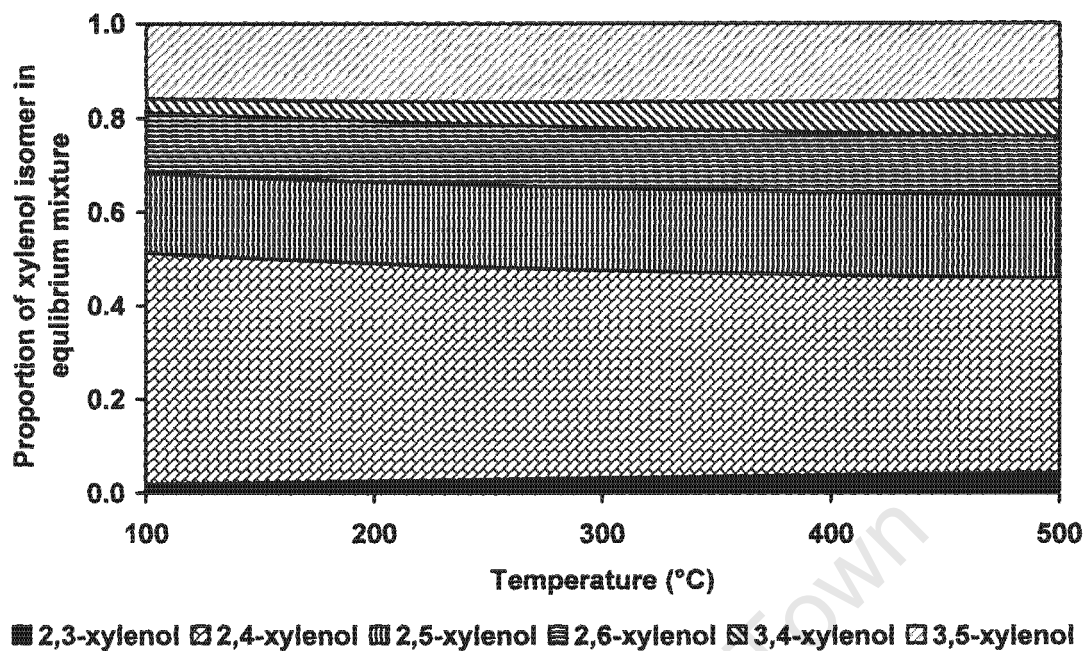


Figure 2-6: Calculated distribution (cumulative) of the xylene isomers in ideal gas phase thermodynamic equilibrium mixture as a function of temperature (see appendix 1, thermodynamic data from Daubert *et al.*, 1999)

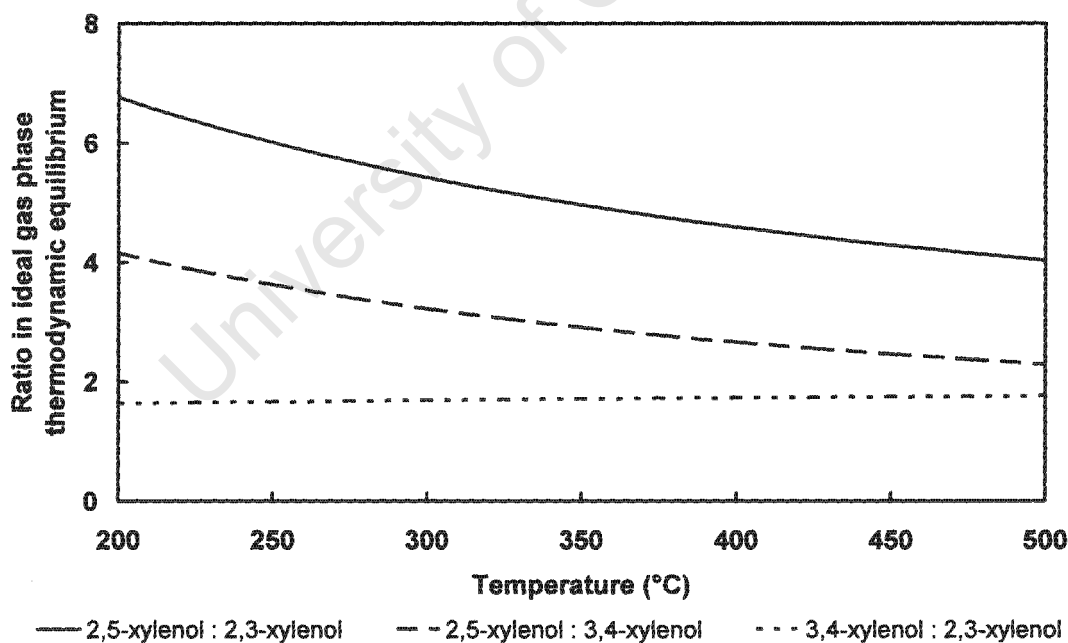


Figure 2-7: Calculated 2,5- : 2,3-xylene, 2,5- : 3,4-xylene and 3,4- : 2,3-xylene ratios in ideal gas phase thermodynamic equilibrium mixture as a function of temperature (see appendix 1, thermodynamic data from Daubert *et al.*, 1999)

Figure 2-8 shows distribution of xylene isomers at thermodynamic equilibrium at 344°C as measured by Pigman *et al.* (1954) compared with that calculated using physical data as published by Daubert *et al.* (1999).

Pigman *et al.* (1954) conducted isomerisation-disproportionation experiments over synthetic silica-alumina. The reaction was carried out in vapour phase and nitrogen was used as diluent. The results shown here were obtained from equilibrium experiments converting pure 2,4-xyleneol and 3,4-xyleneol at 344°C. Starting with 2,4-xyleneol as the reactant, conversion of 88 % was achieved and conversion of 95 % was achieved with reactant 3,4-xyleneol.

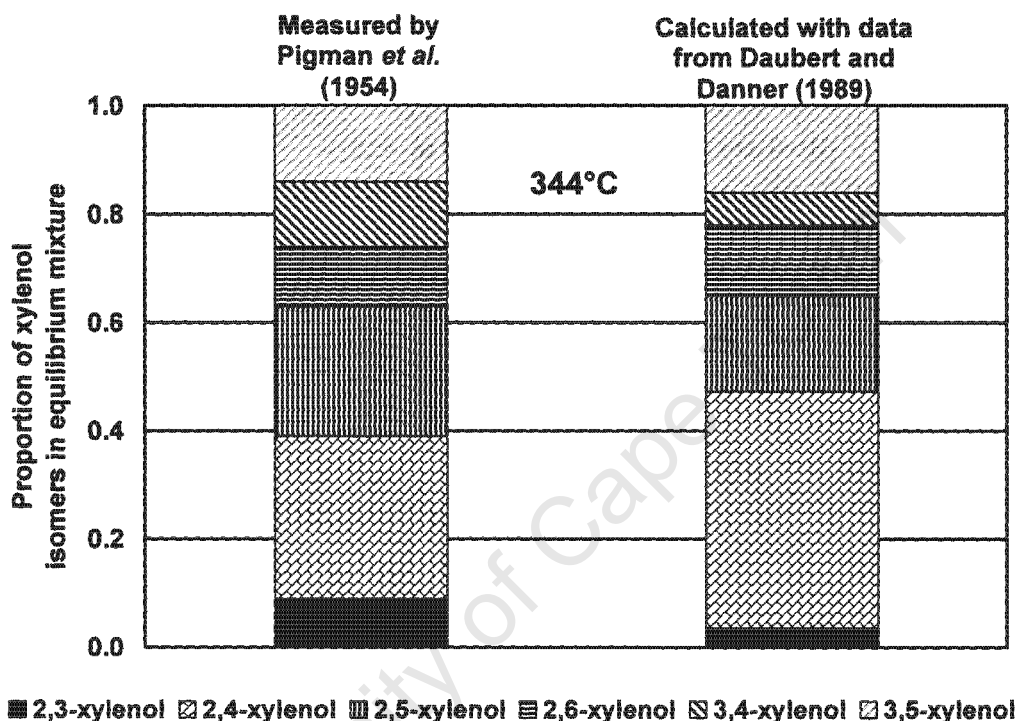


Figure 2-8: Distribution (cumulative) of the xyleneol isomers present in thermodynamic equilibrium at 344°C as measured by Pigman *et al.* (1954) and from thermodynamic calculation using data taken from Daubert *et al.* (1999) (see appendix 1)

Comparison of the two equilibrium distributions shows similarities although the actual proportions vary slightly. However, the measurements confirm that at 344°C 2,4-xyleneol is the most stable isomer, followed by 2,5-xyleneol and then 3,5-xyleneol. The least stable isomer at 344°C is 2,3-xyleneol.

When producing xyleneols at similar temperatures it would be expected that the equilibrated product mixtures show similar distribution to that shown above. However, reaction kinetics and other factors such as using shape selective catalysts and reaction time can be manipulated to generate kinetically controlled product distributions that will differ widely from the equilibrium composition.

Calculated and measured thermodynamic equilibrium distributions of cresols at 380°C are shown in table 2-11. The data show that at 380°C *m*-cresol is the thermodynamically most stable of the cresols and is dominant. Figure 2-9 shows the calculated thermodynamic distribution of cresol isomers for increasing temperatures.

Table 2-11: Thermodynamic equilibrium distributions of cresols at 380°C as calculated using thermodynamic data taken from Stull *et al.* (1969) (see appendix 1) and determined experimentally by Imbert *et al.* (1997) and Fritsch *et al.* (2003)

Isomer	Distribution in gas phase (%)		Distribution in liquid phase (%)
	(Stull <i>et al.</i> , 1969)	(Imbert <i>et al.</i> , 1997)	(Fritsch <i>et al.</i> , 2003)
<i>p</i> -Cresol	4	16	16
<i>m</i> -Cresol	57	48	48
<i>o</i> -Cresol	39	36	36

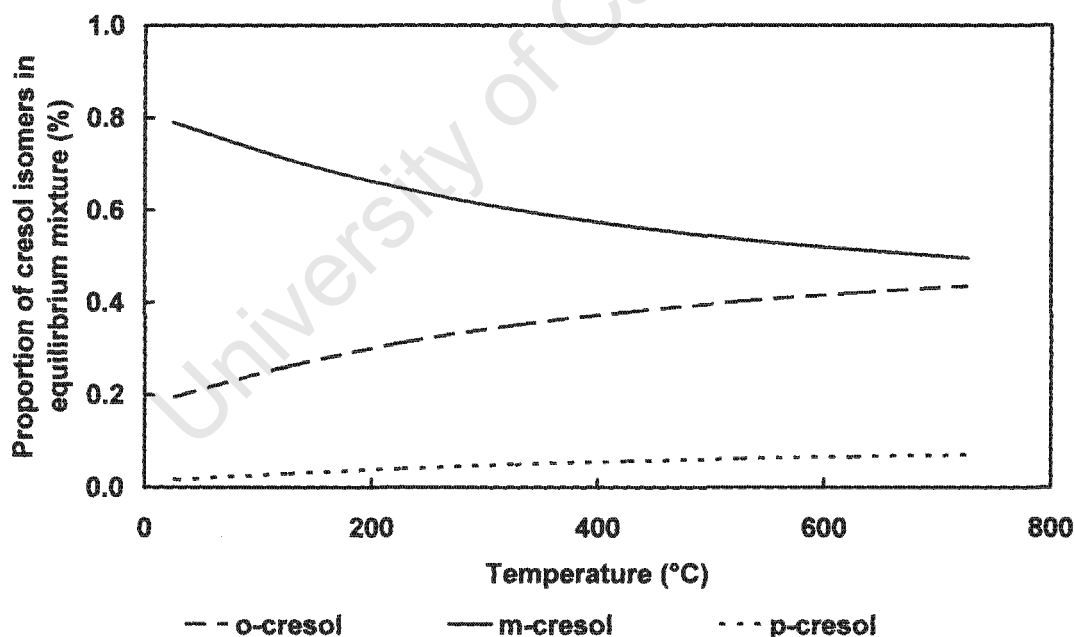


Figure 2-9: Thermodynamic equilibrium distributions of cresols, as a function of temperature, calculated using thermodynamic data taken from Stull *et al.* (1969) (see appendix 1)

2.6.2 Basic kinetics of phenolics methylation

Table 2-12 and 2-13 shows the activation energies of major reactions during phenol methylation with methanol over two alumina catalysts determined between 200°C and 300°C (Tleimat-Manzalji *et al.*, 1993) and over another alumina catalyst (Santacesaria *et*

al., 1990a). The data shows that at lower temperatures, anisole will be the kinetically favoured product, but as temperature increases, more cresol will be produced. It is also clear that, due to its relatively low activation energy, formation of dimethylether will occur at low temperature. Tleimat-Manzalji *et al.* (1993) reported that at methanol conversion of 65 %, approximately 22 % dimethylether was produced (for reaction over an Al_2O_3 aerogel catalyst at 200°C). Formation of dimethylether leads to consumption of methanol. However, the conclusion that this could result in possible starvation of methanol in the reaction must be questioned since dimethylether formation from methanol is reversible (see figure 2-5) and since dimethylether can act as a methylation agent as well (Tleimat-Manzalji *et al.*, 1993).

Table 2-12: Apparent activation energies of major reactions of phenol methylation with methanol over two alumina catalysts (Tleimat-Manzalji *et al.*, 1993)

Catalyst	Apparent Activation Energy (E_A) (kJ / mol)			
	Disappearance of Phenol	Anisole	Formation of <i>o</i> -Cresol	Dimethylether
Al_2O_3 xerogel	121	105	138	71
Al_2O_3 aerogel	117	96	147	80

Table 2-13: Apparent activation energies for reaction of phenol with methanol and of anisole to various products over H-ZSM-5 at reaction temperatures of between 300°C and 331°C (Santacesaria *et al.*, 1990b)

Reactants	Reaction	Apparent activation energy (E_A)
		(kJ / mol)
Phenol + methanol	Overall	50 – 67
	to Anisole	29 – 42
	to Others	80 – 100
Anisole	Overall	67 – 71
	to Phenol	54 – 63
	to Others	88 – 92

Activation energies can indicate whether a particular reaction is diffusion limiting or thermodynamically limited. In general, for activation energies of above 100 kJ / mol, the reaction is usually thermodynamically limited. For activation energies of below 100 kJ / mol, the reaction is often diffusion-controlled (Moon *et al.*, 2004 and Böhringer, 2004).

2.7 Catalysts

Catalysts, via influence on the activation energy of the various reactions, provide the possibility for different reaction pathways or mechanisms, leading to the opportunity for enhanced selectivity of certain products. This is not only useful with regard to maximising yield of the most desired product and thus minimising feed costs, but also in cases where separation and purification costs are high. Different by-products are produced with different catalysts, so catalysts that produce the more useful by-products can be chosen over those producing less useful by-products.

Increased catalytic activity can also mean that a smaller reactor is needed and / or that the reaction can be carried out under milder conditions. Optimum operating conditions differ depending on the catalyst used and through the use of the optimum catalyst, operating costs can be reduced.

While catalysts can be used to accelerate a thermodynamically feasible reaction, they cannot influence the equilibrium of a reversible reaction as the forward and reverse reactions are effected to the same extent (Farkas *et al.*, 2003).

2.7.1 Acid catalysts

Various acid catalysts are used in promoting many different industrial scale reactions. Some of these involve mineral acid catalysts, Friedel-Crafts catalysts or other solid acid catalysts. Following is a very brief discussion of the different acid catalysts employed in industry. Typical reactions that are acid catalysed include hydration-dehydration processes, alkylation, isomerisation, cracking, condensation and cleavage reactions (Farkas *et al.*, 2003).

Solid oxides of the period three elements (Na_2O , MgO , Al_2O_3 , SiO_2 and P_2O_5) are known to show transition from basic to amphoteric to acidic character (Farkas *et al.*, 2003).

Mineral acids, such as HCl , H_2SO_4 are widely used in applications requiring catalysts. The presence of the acid provides protons which are needed in the catalysis of many different processes. During the final stages of the reaction the proton is released back into the solution and becomes available to catalyse another reaction. Section 2.4.2.2 briefly describes the use of H_2SO_4 as a catalyst in the sulphonation of toluene and xylenes.

Friedel-Crafts catalysts can be used in alkylation and acylation reactions. The general mechanism is via electrophilic aromatic substitution. In aromatic alkylation, Friedel-Crafts mechanism requires an aromatic ring, an alkyl halide (e.g. methyl chloride) and a strong

Lewis acid catalyst (e.g. aluminium chloride). One major disadvantage of Friedel-Crafts reactions is that the products are often more nucleophilic than the reactants. This can result in over alkylation of the aromatic molecule (Wikipedia, 2005). In addition, due to increased environmental restrictions, chloro compounds (and chloro catalysts) can be difficult or expensive to dispose of safely.

Until 1990, Union Rheinische Kraftstoff AG in Germany operated a homogenous catalytic phenol methylation process with liquid-phase catalysts, normally zinc halide – hydrogen halide solutions at pressures of 25 bar (a Friedel-Crafts type reaction). The plant had a capacity of 16 000 tonnes / annum and had advantages in that *p*-cresol and 2,4-xyleneol were obtained in considerably larger compositions, and the *p*-cresol was almost free of *m*-cresol. *Para* substitution was increased with increasing methanol feed content, although this was achieved at the expense of lower yield (Fiege, 2003).

Solid acid catalysts (e.g. silica-alumina, see section 2.7.3.2 for further information) are also used widely in catalytic reactions. The solid acid catalysts provide protons that can catalyse the reactions.

2.7.2 Zeolites and molecular sieves

The first zeolite mineral, stilbite, was discovered in 1756 by the Swedish mineralogist Cronstedt. In 1862, the first hydrothermal zeolite synthesis by St. Claire Deville yielded levynite. In 1925, Weigel and Steinhoff reported the selective adsorption by zeolites of some chemicals but not others – in other words the first molecular sieve effect. Later in 1930, Taylor and Pauling determined the first structures of zeolites (Flanigen, 1991).

2.7.2.1 Industrial use

Zeolites have been used as both adsorbents and catalysts in the separation and purification of air, the drying of refrigerant and natural gas, and a major application is as a water softener in household detergents. Union Carbide Corp. began using zeolites to conduct normal – isoparaffin separation in 1959. In 1962 Mobil began using zeolite X as a cracking catalyst and by 1977 some 22 000 tons per annum of zeolite Y were being used in catalytic cracking (Flanigen, 1991). In 1993 the total production of zeolites was approximately 1 200 000 tonnes (Roland *et al.*, 2003).

2.7.2.2 Zeolite use as catalysts

Zeolites can be transformed into hydrogen form, where they are solid acids displaying either Brønsted or Lewis acidity. Acid strength is dependent on the $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio.

Increasing the presence of aluminium in the zeolite framework (i.e. decreasing the $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio) will increase the number of $-\text{OH}$ groups on the framework, but the overall strength of the sites will decrease. The following methods are used industrially to produce Brønsted centres (Roland *et al.*, 2003):

Ion exchange is an important aspect in the synthesis of zeolite catalysts, with the aim of producing Brønsted acid sites. For some zeolites ion exchange of intermediate-silica and high-silica forms can be achieved with mineral acids, although there is a risk of dealuminating the zeolite framework through which high-aluminium species may lose their crystal structure (particularly where high acid concentrations are used). For this reason ion exchange often entails an indirect route, viz exchange with ammonium salt solutions. From the “ammonium form” ammonia is liberated via calcination at ca. 400°C to give the hydrogen form. To produce bifunctional zeolites, which combine acidity with hydrogen-transfer capability, the deposition of metals such as platinum and palladium is important. These metals are also deposited in ammonium form i.e. $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{Pd}(\text{NH}_3)_4]^{2+}$ in this case. Calcination in the presence of oxygen will destroy the ligands and further treatment with hydrogen will lead to the formation of metal clusters. The size of the metal clusters, locations and states of deposition are dependent on the conditions (Roland *et al.*, 2003).

Zeolites are widely used in the following areas.

2.7.2.2.1 Oil refining

Zeolites are used in several different oil refining applications. The most important of these is in Fluidised Catalytic Cracking (FCC), where zeolites are employed to convert vacuum distillates and residues into gaseous alkenes and alkanes, gasolines and diesel fuel. Zeolites are preferred to silica-alumina (which, previously was used widely) as a cracking catalyst due to their higher activity, higher gasoline yield and lower coke formation. USY (ultra stable Y) zeolite is the most popular zeolite in this application, largely due to its large pore size and its increased stability at higher temperatures (Roland *et al.*, 2003).

Zeolites are also utilised in hydrocracking applications. In this process higher boiling Gas Oils or residues are converted, in the presence of hydrogen, into more useful fuels, mainly kerosene and diesel. USY zeolites, doped with a hydrogenation / dehydrogenation function in the form of a metal (e.g. platinum) are widely used. The catalysts must be protected from sulphur and nitrogen, which act as poisons, so a reactor with an HDS (hydrodesulphurisation) and HDN (hydrodenitrogenation) catalyst must be operated upstream (Roland *et al.*, 2003).

An important process in oil refining is the isomerisation of C_5 / C_6 *n*-alkanes. This is normally done with Pt / H-mordenite or H-ZSM-5. Shell has combined this process with the adsorptive separation of *n*- and iso-alkanes and recycling of the former. This is known as the TIP process (total isomerisation process) (Roland *et al.*, 2003).

Research is underway to investigate the opportunity to use zeolites Pt / K-L and Pt / BaK-L in dehydrocyclization of C_6 / C_7 alkanes. Conventional reforming catalysts show poor selectivity for species in this range. However, at this stage the new catalysts are sensitive towards sulphur poisoning. It is reported that H-ZSM-5 is used in post-reforming operations. This entails shape-selective cracking of *n*-alkanes with simultaneous alkylation of benzene and toluene with the short-chain alkenes that are produced (Roland *et al.*, 2003).

2.7.2.2.2 Conversion of gases

Zeolites are used in the context of converting synthesis gas and LPG (liquefied petroleum gas) into liquid fuels. Mobil have designed a process that converts methanol (made from syngas) to gasoline (MTG) using zeolite ZSM-5. ZSM-5 initially converts methanol into the intermediate dimethylether and then into short chain alkenes. Further chain growth occurs and aromatics and low alkanes are produced by cyclisation and hydrogen transfer. Other similar processes are also reported (Roland *et al.*, 2003).

In South Africa, PetroSA use zeolite based catalysts in the conversion of olefins to diesel (COD). Through this process PetroSA is able to produce very high quality diesel with low sulphur content (< 5 ppm) and a low freezing point (< -34°C) (PetroSA, 2005).

2.7.2.2.3 Petrochemistry and synthesis of organic intermediates

Research into the production of petrochemicals using zeolites has intensified. This has been motivated, in part, by increasing pressure on existing processes that use acid catalysts such as H_2SO_4 , HF, H_3PO_4 on silica and $AlCl_3$. Use of these acids creates high costs and environmental concerns as they are corrosive, while the zeolite catalysts are not, and are usually less selective. Typical processes that use zeolites in this way include alkylation of aromatics, disproportionation of alkyl- and chlorobenzenes, isomerisation, oligomerisation and hydration of alkenes and formation of amines from alcohols and ammonia. Some of these processes are listed in table 2-14 (Roland *et al.*, 2003).

Table 2-14: Various petrochemical processes that use zeolites to produce organic intermediates, the zeolite used and the process developer (Roland *et al.*, 2003)

Process	Zeolites Used	Process Developer
Production of ethylbenzene from benzene and ethylene	H-ZSM-5	Mobil-Badger
Production of cumene from benzene and propene (liquid phase)	H-Y	Chemical Research & Licensing Co.
Production of <i>p</i> -ethyltoluene from toluene and ethylene	Modified ZSM-5	Mobil
Isomerisation of xylene	Pt/H-ZSM-5 Pt/H-Mordenite	Mobil and others
Disproportionation of toluene to produce xylene	H-Mordenite, ZSM-5	Mobil UOP / Toray
Amination of methanol by ammonia, producing dimethylamine as the principal product	Na / H-Mordenite	Nitto
Hydration of cyclohexene to cyclohexanol	H-ZSM-5	Asahi
Production of pyridine from acetaldehyde, formaldehyde and ammonia	H-ZSM-5	Nepera
High-purity isobutene from MTBE	H-ZSM-5	Snamprogetti
Ammonoxidation of cyclohexanone to cyclohexanone oxime*	Titanium silicate-1	Enichem
Hydroxylation of phenol to hydroquinone / catechol*	Titanium silicate-1	Enichem

**These processes have been phased out*

2.7.2.2.4 Detergent Builders

The most important application of synthetic zeolites in recent years has been in detergent building. Detergent builders represent the largest use of zeolites, accounting for approximately 90 % (or 1 050 000 tonnes) of the zeolites produced in 1994. Of this, 950 000 tonnes of zeolite NaA was produced with the remaining 100 000 tonnes comprising zeolite NaP (Roland *et al.*, 2003).

Zeolite NaA has been employed as a detergent builder since the 1970s. Zeolite NaA has been favoured over the traditional phosphate based detergents (e.g. pentasodium tripolyphosphate) due to the fact that it doesn't contain phosphates. The major disadvantage with the traditional detergent builders, such as pentasodium tripolyphosphate, was that concentrations of phosphates in surface waters was causing ecological problems, including over fertilisation, eutrophication, excessive growth of algae,

which can eventually lead to lower oxygen levels within the surface waters (Roland *et al.*, 2003).

The search for a replacement for phosphate based detergent builders lead to the development of zeolite NaA. It was important that the zeolite be of average particle size ca. 3.5 μm to prevent incrustations in the textile fibres. The main function of the detergent builder is to bind ions that cause hardness and the capacity for ion exchange is measured with respect to Ca^{2+} (which is present in much higher concentrations than Mg^{2+}). The use of zeolites as detergent builders has a positive side effect. Heavy metals, e.g. Cu^{2+} , which may be present in trace amounts, are absorbed by the zeolites (Roland *et al.*, 2003).

Importantly, extensive investigations into the effect of zeolite NaA on surface water systems have shown no harmful effects (Roland *et al.*, 2003).

2.7.2.2.5 Others

Natural zeolites are used in bulk applications of paper production, in pozzolanic cements and concretes, in fertilizers and soil conditioners, in water treatment applications and as dietary supplements in animal husbandry (Flanigen, 1991).

2.7.2.3 Zeolite compositions and structure

Zeolites are essentially crystalline aluminosilicates comprising group IA and group IIA elements.

Zeolites have complex, crystalline inorganic polymer structures based on extended three-dimensional, four-connected frameworks of AlO_4 and SiO_4 tetrahedra linked to each other through shared oxygen atoms. The AlO_4 tetrahedra exhibit a single negative charge, while the SiO_4 tetrahedra exhibit no charge. The negative charges are balanced by cations, which are highly mobile and are ordinarily accessible to undergo ion exchange (Flanigen, 1991).

The structural formula of a zeolite is represented by:



with x and y the total number of tetrahedra contained per unit cell, n being the valance of the charge balancing cation M and w being the content of water molecules per unit cell. y / x Ratios may range from 1 (for zeolite X) to ∞ (for silicalite). According to the Loewenstein Rule, $\text{Al}-\text{O}-\text{Al}$ groups cannot occur so $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratios of less than 2 are not possible (Roland *et al.*, 2003). Water may be removed, generally done through

applying heat, leaving an intact crystalline host structure permeated by micro-pores and voids, which may account for up to 50 % of the total volume (Flanigen, 1991).

Generally there are two types of pore systems in zeolites (Flanigen, 1991):

1. A system comprising interconnected cage-like voids
2. A system of uniform channels, in this case one-dimensional, two-dimensional and three-dimensional channel systems that can be interconnected or not. Usually, in adsorption and catalytic applications, two- and three-dimensional interconnected channel systems are preferred as rapid intracrystalline diffusion can take place.

Combinations of the two types are known, e.g. MCM-22.

It has been reported that over 100 distinct frameworks of zeolites and zeotypes are known, with pore sizes ranging from 0.3 nm through to 0.8 nm and pore volumes ranging from 0.10 to 0.35 cm³ / g (IZA, 2005 and Flanigen, 1991).

Zeolites are often classified according to their pore size (i.e. small, medium or large pores). Small pore zeolites typically have eight-ring pores (i.e. built from eight oxygen atoms) with free diameters of 0.30 – 0.45 nm (e.g. zeolite A). Medium pore zeolites generally comprise ten-ring pores with a free diameter of 0.45 – 0.60 nm (e.g. zeolite ZSM-5) while large pore zeolites comprise a twelve-ring pore with free diameter of ~0.8 nm (e.g. zeolites X and Y) (Flanigen, 1991 and Roland *et al.*, 2003).

Figure 2-10 shows a comparison between different zeolite pore size and the kinetic diameter of different common compounds at room temperature (Roland *et al.*, 2003).

The zeolite structure is somewhat flexible, with the pore and framework size and shape dependant on temperature and guest species. The zeolite framework undergoes thermal vibrations that will fractionally alter the effective pore size and thus allow molecules with similar kinetic diameters to pass through the pore. Therefore the selectivity of molecules, whose diameters are similar to that of the zeolite pore size and which may pass through the zeolite pore, is dependent on the temperature (Roland *et al.*, 2003).

Presence of an adsorbate changes pore size and shape. It has been observed that ZSM-5 has near circular pores with diameter of 0.62 nm with neopentane as the sorbed species, but elliptical pores with diameter of 0.45 to 0.70 nm when substituted aromatics are sorbed (Flanigen, 1991). The sorbed species can also affect the geometry of the zeolite pores.

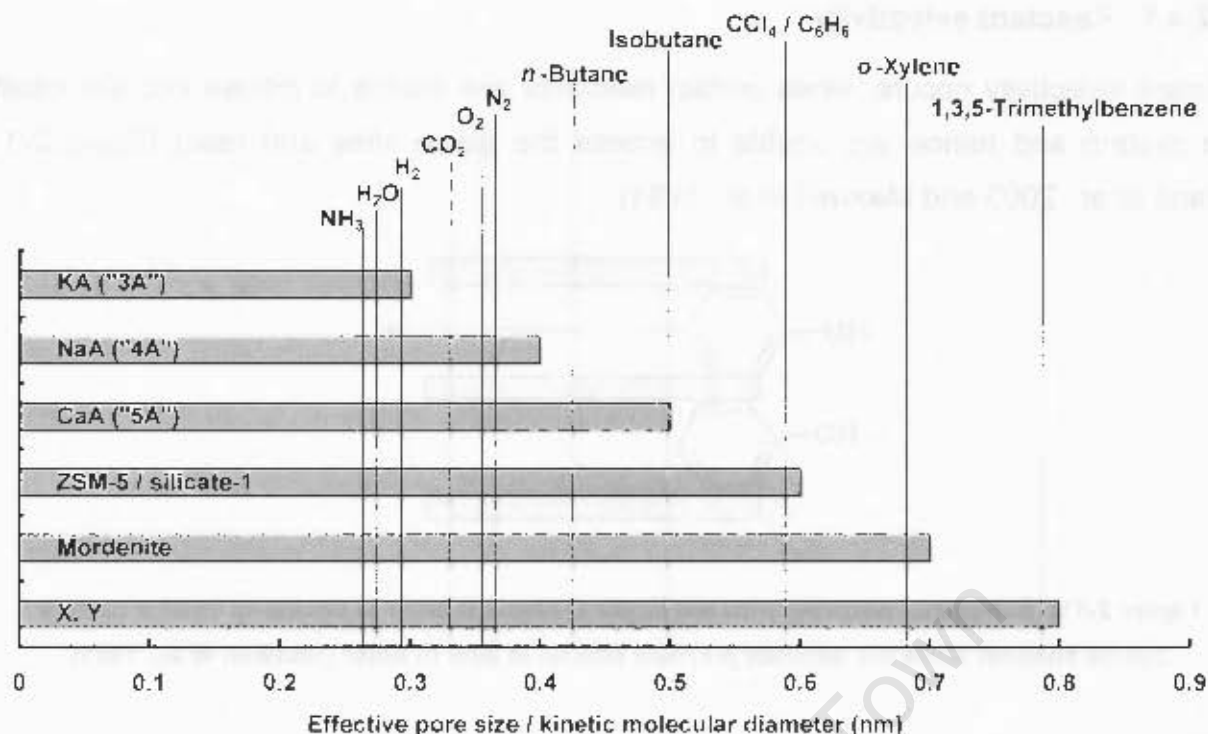


Figure 2-10: Correlation between the effective pore size of industrially important zeolites and the kinetic molecular diameter of selected compounds (at room temperature) (Roland *et al.*, 2003)

Researchers found that monomolecular reactions are favoured in 10-ring zeolites (H-ZSM-5 in this case) and bimolecular reactions are favoured in 12-ring zeolites (H-Y). This is due to pore size and void volume constraints. This was confirmed in methylation of anisole, where selectivity of *p*-cresol, a secondary product obtained through a bimolecular transalkylation reaction, was compared to selectivity to *o*-cresol, a primary product formed in intramolecular rearrangement reaction. Formation of *p*-cresol was suppressed when the reaction occurred over H-ZSM-5 other than over H-USY where *p*-cresol was formed (Parton *et al.*, 1989).

2.7.2.4 Shape selectivity

Shape selectivity is the phenomenon where the selectivity of reactions is influenced or controlled by geometric constraints. The shape selectivity effect in reactions is very similar to the molecular-sieve effect seen in adsorption. Shape selectivity may occur where the sizes of the zeolite pores are of similar dimension to those of the molecules or transition states present in the reaction. The phenomenon was first described by Csicsery. With zeolites, this phenomenon manifests in the following three forms (Roland *et al.*, 2003 and Maxwell *et al.*, 1991):

2.7.2.4.1 Reactant selectivity

Reactant selectivity occurs, when certain reactants are unable to diffuse into the zeolite pore system and hence are unable to access the active sites and react (figure 2-11) (Roland *et al.*, 2003 and Maxwell *et al.*, 1991).

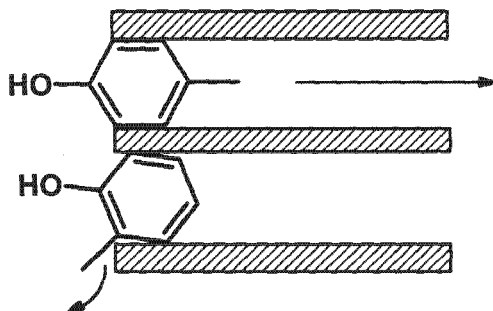


Figure 2-11: Schematic showing how the larger *o*-cresol isomer is unable to enter a narrow zeolite channel while the slimmer *p*-cresol isomer is able to enter (Maxwell *et al.*, 1991)

2.7.2.4.2 Product selectivity

In product selectivity, the reaction takes place in the pore, but certain products that may form within the wider sections of the zeolite pore system (channel intersections or voids) are unable to exit the zeolite crystal due to their bulky nature. These products remain in the wider sections of the pore system undergoing further reaction, e.g. isomerisation, until a product is obtained which can diffuse out of the pore system (figure 2-12) (Roland *et al.*, 2003 and Maxwell *et al.*, 1991). Note that this requires a reaction mechanism for interconversion of the product molecules, e.g. forming an equilibrium pool of compounds, such as isomers inside the zeolite crystal (Olson *et al.*, 1984).

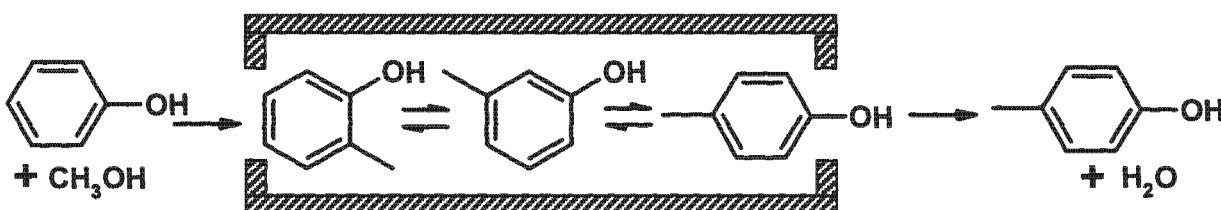


Figure 2-12: Schematic showing the formation of an internal isomer equilibrium pool. The more bulky *o*- and *m*-cresol isomers are unable to exit the narrow zeolite channel while the slimmer *p*-cresol isomer is able to exit (Maxwell *et al.*, 1991)

Often product selectivity is not based on a “go” and “no go” system, but just on differences of the diffusion coefficients. In such systems, the Thiele Modulus of the unwanted reactions must be high enough to cause an effect.

The Thiele modulus relates k , the rate of reaction with D , the effective diffusivity (see equation 2-1). Normally k will show more variation with increasing temperature than D . The relationship is discussed in more detail in section 2.9.2.

Equation 2-1: Relationship of the Thiele Modulus with rate of reaction, k and effective diffusivity (Fogler, 1999).

$$\varphi \approx R \sqrt{\frac{k}{D}}$$

2.7.2.4.3 Transition-state selectivity

In restricted transition-state selectivity there is only sufficient space in the pore system for certain non-bulky reaction intermediates or transition states (figure 2-13). Products which form via bulky intermediates are not produced. In the first schematic the intermediate is more bulky than the zeolite cage or channel intersection width and hence this reaction will not occur. The second reaction entails the formation of an intermediate that is slim enough to fit within the zeolite cage, so this reaction will progress and the respective compound will be produced (Roland *et al.*, 2003 and Maxwell *et al.*, 1991).

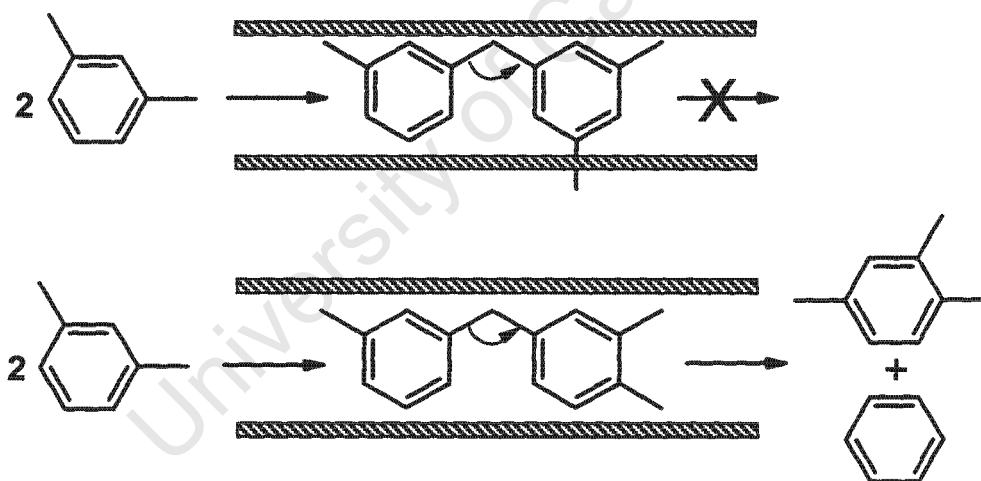


Figure 2-13: Schematic showing how the more bulky transition state is unable to form within the narrow zeolite channel while the slimmer transition state is able to form (Maxwell *et al.*, 1991)

2.7.3 Catalysts to be used in this study

2.7.3.1 Zeolites investigated

In this study, the methylation of a cresol isomer was studied with the intention to affect transport control on the products, i.e. product shape selectivity. Thus, the performance of a number of zeolites was investigated. Following is a brief description of the zeolites used (IZA, 2003). See table 2-15 for further details.

1. ZSM-5 (MFI) is a medium pore zeolite. It has two perpendicularly intersecting 10 membered-ring channels, one being a circular sinusoidal channel with almost round openings of diameter 0.54 x 0.56 nm and the other being a straight channel with elliptical pores of diameter 0.52 x 0.58 nm (IZA, 2003). The sinusoidal channels connect two parallel layers of straight channels in a staggered way so that the pore system of ZSM-5 is in fact also open for diffusion of molecules in the third dimension through constant altering between channel systems. The intersection of these channels is somewhat offset and has a critical dimension of 0.9 nm (Santacesaria *et al.*, 1990). Geometric constraints imposed by the 10 ring pores hinder internal coke formation since large polynuclear hydrocarbons, coke precursors, have difficulty forming.
2. Ferrierite (FER) is a medium pore zeolite. It has 2 channels of differing size. One channel, comprising 8 ring pores, has dimensions 0.35 x 0.48 nm. The other channel, comprising 10 ring pores, is larger with dimensions of 0.42 x 0.54 nm (IZA, 2003). The widest channel in FER is a little smaller than the channels of ZSM-5 and mono-dimensional. The other channel does not allow access to aromatic molecules.
3. ZSM-12 (MTW) is considered a large pore zeolite. It has two intersecting channels that are of identical size, of 0.56 x 0.60 nm, with each comprising 12 atoms in structure (IZA, 2003). The channels of MTW are slightly wider than the widest channel of MFI.
4. Mordenite (MOR) is a large pore zeolite. It has a two dimensional channel system, of which one channel comprises a 12 membered ring, with dimensions of 0.65 x 0.70 nm, and the other of an 8 membered ring, with dimensions of 0.26 x 0.57 nm (IZA, 2003). The only channel that is accessible to aromatic molecules is the large, straight, 12-membered ring channel.
5. H-Beta (BEA) is a large pore zeolite. It has three intersecting channels, each comprising 12-membered rings. Two channels are straight and 0.66 x 0.67 nm wide, while the third channel is sinusoidal and 0.56 x 0.56 nm wide. In the pore system, all three channels cross at the same point (IZA, 2003).

Table 2-15: Properties of the zeolites used (IZA, 2003)

IZA code	Common name	No of channels	Number of T-atoms*	Size (Å)	Inter-connections	Dimensionality of pore system**
MFI	ZSM-5	2	10 10	5.1 × 5.5 5.3 × 5.6	Yes	3
FER	Ferrierite	2	8 10	3.5 × 4.8 4.2 × 5.4	Yes	1
MTW	ZSM-12	2	12 12	5.6 × 6.0 5.6 × 6.0	Yes	2
MOR	Mordenite	2	12 8	6.5 × 7.0 2.6 × 5.7	Yes	1
BEA	Beta	3	12 12 12	6.6 × 6.7 6.6 × 6.7 5.6 × 5.6	Yes	3

*Number of T atoms forming pore opening, T atoms are either Si or Al

**Effective dimensionality for diffusion of monoaromatics

Balsama *et al.* (1984) screened several zeolites for methylation of phenol in a fixed-bed continuous reactor at 250°C, finding that amongst H-Y, H-ZSM-5, H-X and others, H-ZSM-5 displayed very low activity. For similar reaction conditions, the phenol conversion achieved over H-ZSM-5 (1.1 %) was much lower than that achieved over H-Y (46.9 %) (Balsama *et al.*, 1984).

H-ZSM-5 showed low selectivity to 'C' alkylation, with an initial cresol selectivity of 27 mol % (the initial selectivity to anisole was 73 mol %). In contrast zeolite H-Y yielded a surprisingly high initial selectivity to cresol (53 mol %) compared to anisole (9 mol %). The selectivity changed with time-on-stream to 40 mol % cresol and 50 mol % for anisole after 7 h. They also found initial selectivity to xylenols was about 15 % (Balsama *et al.*, 1984). However, these may mainly be conversion effects since anisole is an intermediate.

2.7.3.2 Amorphous silica-alumina (Siral)

Silica-alumina is amorphous in nature, in that it does not exhibit any clear crystal structure. Like many zeolites, silica-alumina comprises silicon, aluminium and oxygen, however, unlike zeolites there are no defined channels or uniform pores of any sort.

When silica-alumina is treated with strong acids, such as hydrochloric or hydrofluoric acids, the material acts as a solid acid. It becomes capable to promote reactions requiring

acid catalysis. Under these circumstances, when trivalent aluminium is forced by surrounding tetravalent silicon to crystallise in a tetrahedral symmetry, a partial electron deficiency occurs at the aluminium site allowing it to act as a Lewis acid, or react with water to form conjugated Brønsted sites (Wikipedia, 2005).

Siral is a type of silica-alumina hydrate produced by Sasol Germany. Dopants are used to enhance the thermal stability of the catalyst and increase the relative acidity. Silica-alumina hydrate is a suitable carrier for catalytic processes where surface acidity is required to enhance the catalytic activity (Sasol, 2005).

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2.8 Mechanisms of the acid catalysed reactions involved

Substituting silicon in silica with ions with lower charges than Si^{4+} , can create acid sites. Acid catalysed reactions, as in H-zeolites or amorphous silica-alumina, proceed via the donation of a proton (H^+ ion) from the catalyst structure to the reactant or the abstraction of an electron rich species, e.g. a hydride anion from the reactant.

A catalyst has Brønsted acidity if it is able to donate a proton. A Lewis acid is a compound that can accept an electron pair. A Brønsted acid may be transformed into a Lewis acid through heating and driving off water, as shown in figure 2-14 (Santacesaria *et al.*, 1990b).

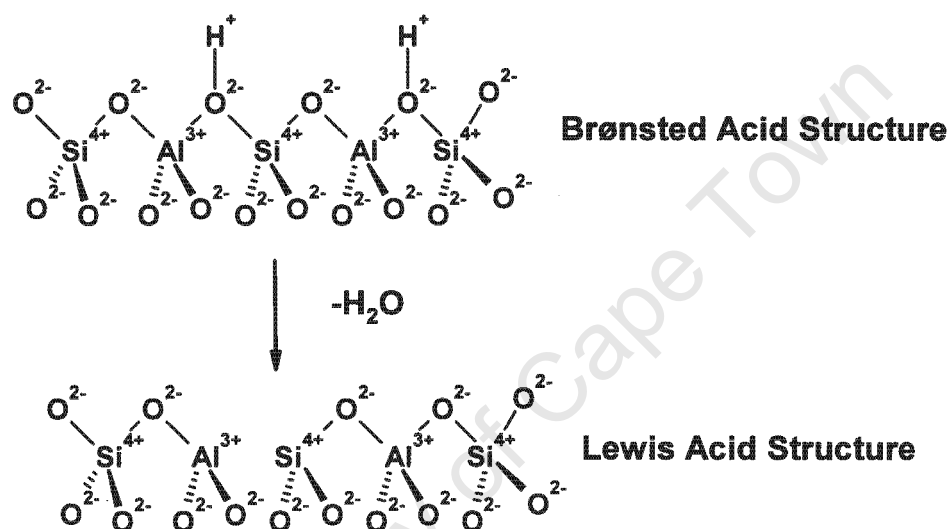


Figure 2-14: The transformation from a Brønsted acid structure to a Lewis acid structure with the loss of water (Santacesaria *et al.*, 1990b)

With higher silica : alumina ratios, the proportion of aluminium drops and there are fewer acid sites available. Although higher silica : alumina ratios provide fewer acid sites, the acid sites are comparatively stronger. In contrast, lower silica : alumina ratios provide more acid sites but, the acid sites are weaker (Flanigen, 1991).

Following are reaction mechanisms for the formation of dimethylether from methanol, xyleneol from cresol, methylanisole from cresol and methylanisole rearrangement to xyleneol over Brønsted acid sites. Also included are mechanisms for the formation of products over silica-alumina (with Brønsted and Lewis acid sites), as proposed by Santacesaria *et al.* (1990a).

In the following diagrams, $\text{H}^+ \text{Z}^-$ represents a Brønsted acid catalyst i.e. with an available proton.

2.8.1 Dimethylether formation mechanism

It is known that dimethylether will be formed as a side reaction to the main alkylation reaction (Marczewski *et al.*, 1988 and Tleimat-Manzalji *et al.*, 1993).

Initially dimethylether is formed as two methanol molecules react with each other (figure 2-15). One of the methanol molecules is protonated, forming an active carbenium ion that is attracted to the carbon atom within the second methanol molecule. Thus dimethylether is formed.

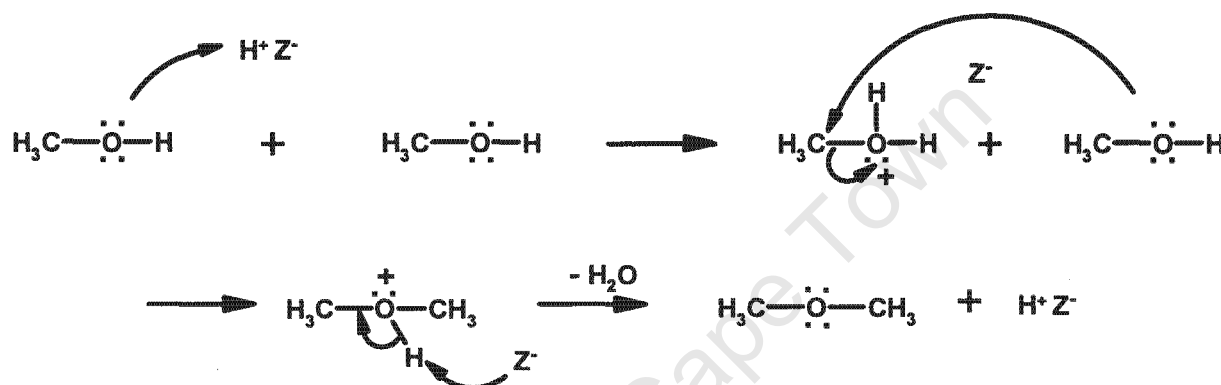


Figure 2-15: Mechanism of formation of dimethylether from methanol (adapted from Marczewski *et al.*, 1988, Sykes, 1986 and Tleimat-Manzalji *et al.*, 1993 and modified)

In tests to determine the feasibility of dimethylether as an intermediate in phenol methylation, dimethylether was reacted with phenol over H-Y at 250°C. Results showed that dimethylether is much less reactive than methanol under similar reaction conditions. Thus it was suggested that dimethylether is not a reaction intermediate (Balsama *et al.*, 1984). However, this was not investigated over other catalysts.

2.8.2 Mechanism for carbenium ion formation from methanol and dimethylether

Literature suggests that alkylation of phenol or cresol by methanol or dimethylether is initiated by the formation of carbenium ions. The carbenium ion is formed when a proton (H^+), present on the acidic catalyst, is attracted to the electron pairs on the oxygen atom (see figure 2-16). The positive charge (due to the absorbed proton), centres about the oxygen atoms (Sykes, 1986 and Marczewski *et al.*, 1988).

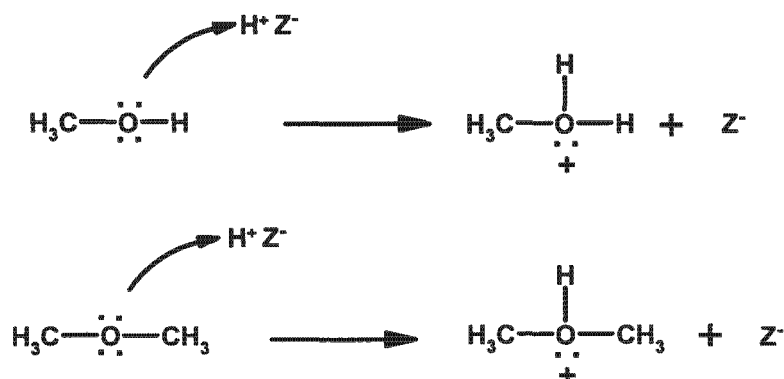


Figure 2-16: Mechanism for the protonation of methanol and dimethylether (Sykes, 1986 and Marczewski *et al.*, 1988)

2.8.3 Mechanism for xylenol formation from *m*-cresol and methanol via a carbenium ion intermediate

In this mechanism 2,5-xylenol is formed from *m*-cresol via a carbenium ion intermediate. In this mechanism methanol is used as the alkylating agent. Methanol, being more basic than cresol, is absorbed onto the protonic centres as $\text{CH}_3\text{O}^+\text{H}_2$ (Marczewski *et al.*, 1988).

The intermediate carbenium ion then reacts with the *m*-cresol ring, to produce a xylenol molecule (figure 2-17). Kinetically the preferred position for the methyl group on which to bond is the *ortho* position, and the least preferred position is the *meta* position. *Para* preference is very similar to *ortho* preference, but as there are two *ortho* positions, statistically more *ortho* product than *para* product is produced. The delocalization of electrons within the phenol molecule stabilizes the transition state, particularly for *ortho* and *para* alkylation, in such an alkylation reaction (Sykes, 1986).

The '2' *ortho* position in *m*-cresol is less likely to be methylated than the '6' *ortho* position as there will be a degree of steric hindrance caused by the methyl group in the *meta* (or '3') position and the hydroxyl group in the primary position. The second *meta* position faces strong resistance to methylation (at mild conditions) as it is less reactive than the other positions (adapted from Sykes, 1986).

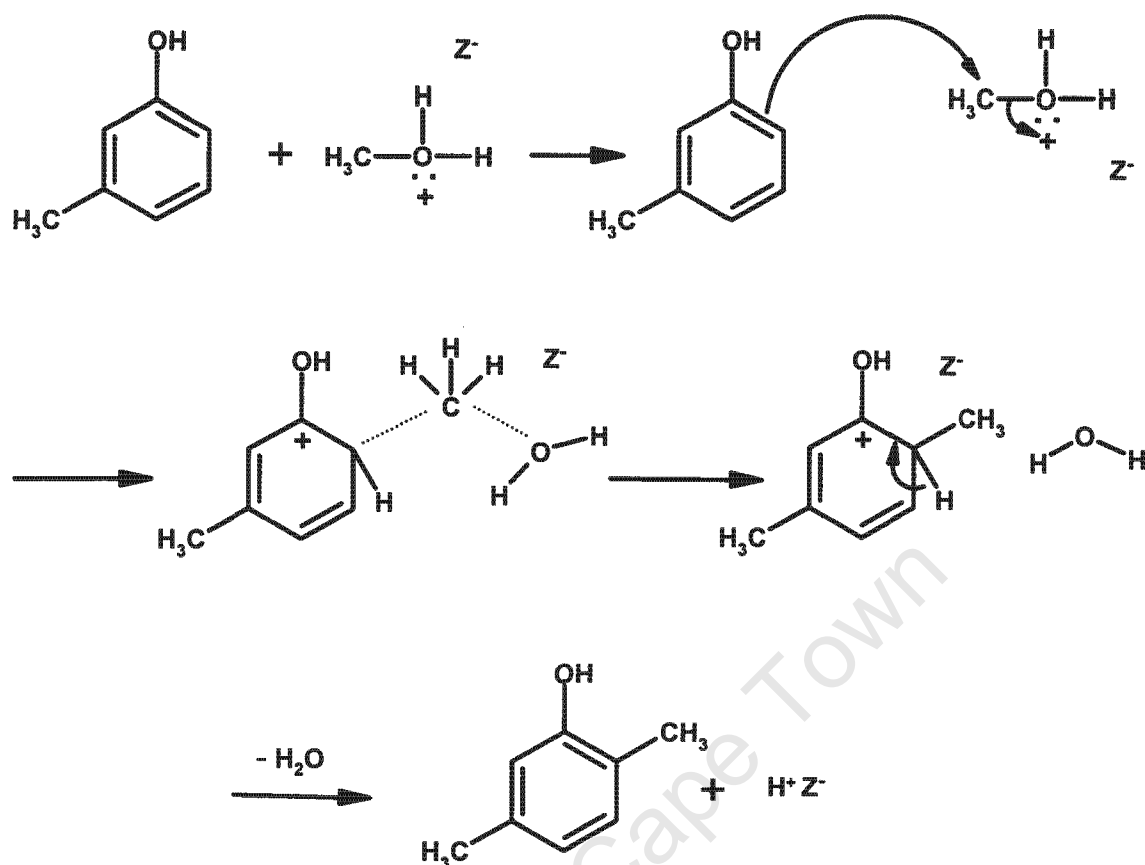


Figure 2-17: Mechanism for formation of 2,5-xyleneol from *m*-cresol reaction with methanol (via carbenium ion intermediate) over an acid catalyst (adapted from Marczewski *et al.*, 1988, Moon, 2003 and Sykes, 1986)

2.8.4 Xylenol formation via dimethylether intermediate mechanism

The formation of xylenol isomers via a dimethylether intermediate has also been suggested (Marczewski *et al.*, 1988 and Moon, 2003). The formation of dimethylether from methanol is discussed in section 2.8.1.

Dimethylether reacts with *m*-cresol by a similar mechanism as described for the reaction of *m*-cresol with methanol in section 2.8.3. Initially the oxygen atom in the dimethylether molecule is protonated forming an active carbenium ion (figure 2-18). This is attracted to the electro-negative ring of the cresol and reaction on one of the ring carbons is initiated. The cresol ring, being more electro-negative than the oxygen molecule in the dimethylether ion attracts the CH₃ group in the dimethylether strongly, resulting in a weak bond between the oxygen and CH₃ group. The OH-CH₃ group is cleaved off, forming another methanol molecule and leaving a xylenol molecule as the product (adapted from Moon, 2003 and Sykes, 1986).

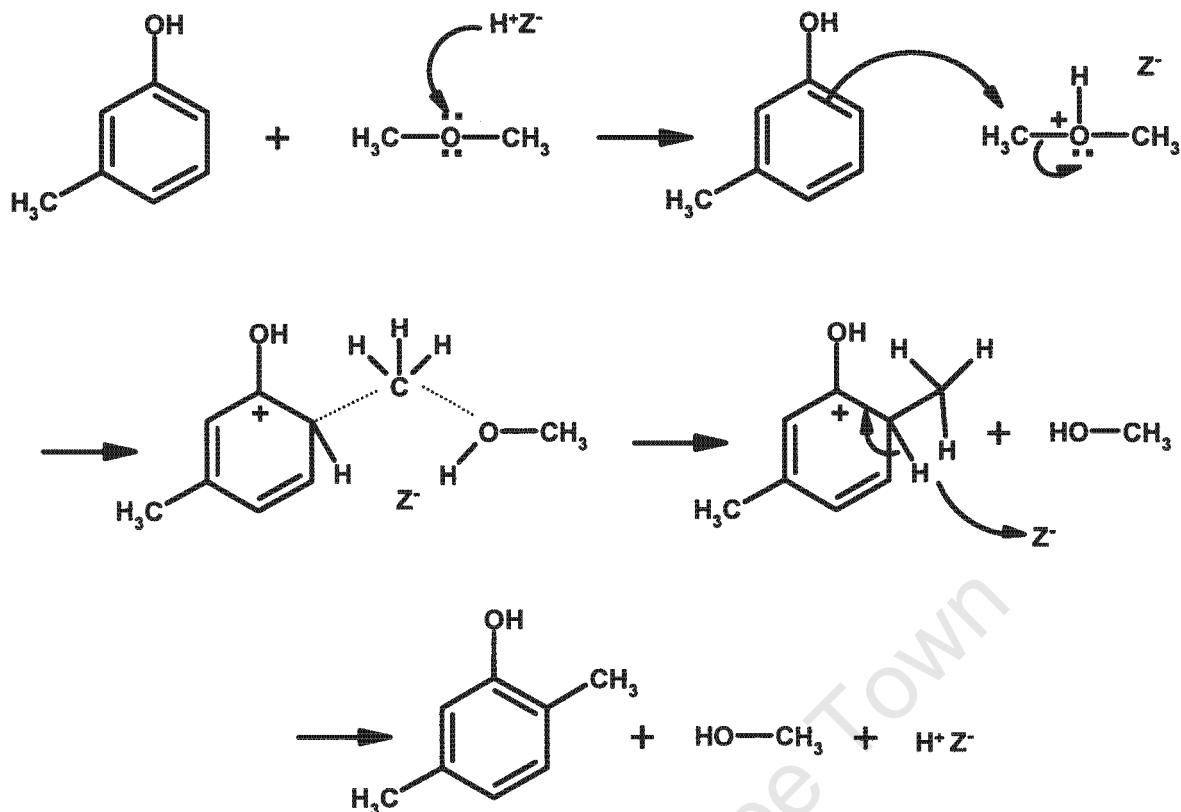


Figure 2-18: Mechanism of formation of 2,5-xyleneol from *m*-cresol reaction with dimethylether (via a carbenium in intermediate) over an acid catalyst (adapted from Marczewski *et al.*, 1988, Moon, 2003 and Sykes, 1986)

2.8.5 Xylenol formation via a methylanisole intra-molecular rearrangement mechanism

The production of xylenols via the formation of 3-methylanisole as an intermediate is proposed. In this mechanism, 3-methylanisole is produced via 'O' alkylation (figure 2-19) and then undergoes intramolecular rearrangement to form 2,3- or 2,5-xyleneol (figure 2-20). Similar mechanisms for the formation of *o*-cresols from phenol methylation via an anisole intermediate have been suggested in literature (Balsama *et al.*, 1984, Marczewski *et al.*, 1988, Moon, 2003 and Santacesaria *et al.*, 1990a and 1990b). It was observed that this is particularly favoured over 10 membered ring rather than over 12 membered ring zeolites and over zeolites with lower Brønsted acid strength (Parton *et al.*, 1989).

Initially, methanol is protonated and an active carbenium ion formed (see section 2.8.2). The carbenium ion is attracted by the electro-negativity of the oxygen atom on the *m*-cresol molecule. 3-Methylanisole is formed as the carbenium ion forms a bond with the oxygen atom (Parton *et al.*, 1989 and Moon, 2003).

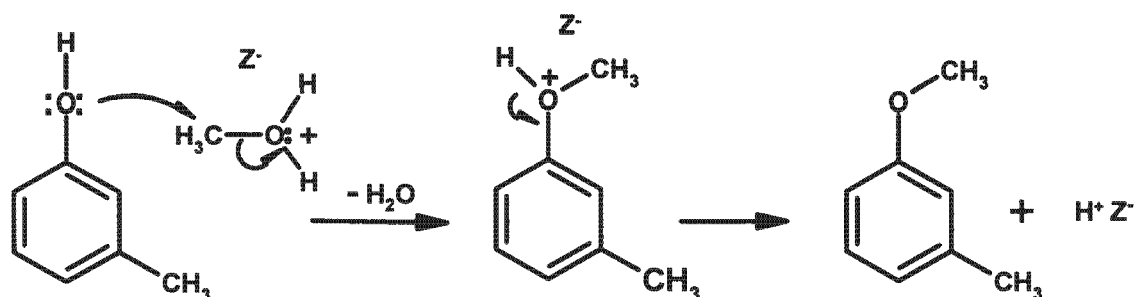


Figure 2-19: Mechanism for formation of 3-methylanisole from methylation of *m*-cresol over an acid catalyst (Parton *et al.*, 1989 and Moon, 2003)

3-Methylanisole undergoes intra-molecular isomerisation in the presence of an acid catalyst, initially forming a carbenium ion intermediate (figure 2-20). 2,3- or 2,5-xylenol is formed as the proton is cleaved off the ring. *Ortho* substitution is most likely as the methyl group is closest to the *ortho* position. 2,5-Xylenol is the most likely product since the 2-position is sterically hindered (Sykes, 1986).

As the reaction temperature increases there is more energy available and internal methylanisole rearrangement as well as direct ring methylation (see sections 2.8.3 and 2.8.4) become more prevalent. Indeed, literature reports the disappearance of anisoles from the product with increasing reaction temperature (Santacesaria *et al.*, 1990b and Moon, 2003).

Note that anisole or methylanisole isomers are thermodynamically much less favoured when compared with the corresponding cresol or xylenol isomers. With the knowledge that 3-methylanisole is an intermediate in the formation of xylenol isomers, there may be an opportunity to recycle any 3-methylanisole product for further conversion into xylenol.

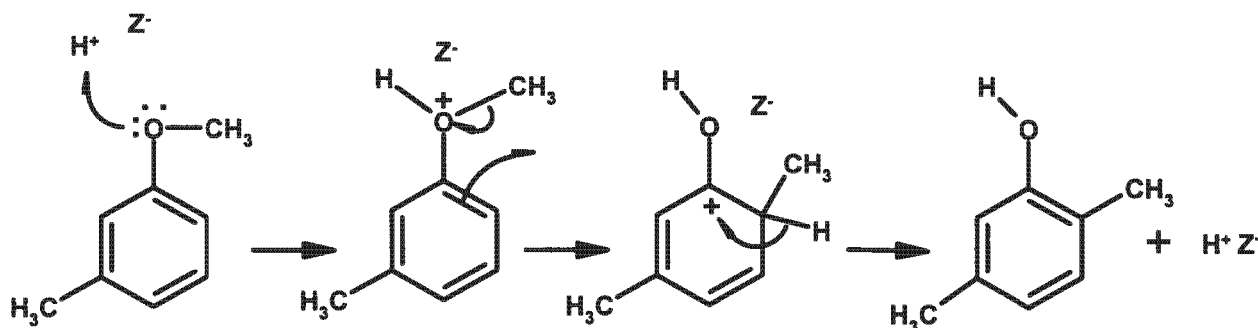


Figure 2-20: Mechanism of formation of 2,5-xylenol from 3-methylanisole on an acid catalyst (adapted from Santacesaria *et al.*, 1990 and Moon, 2003)

It has also been suggested that anisole can react as an intermediate in the alkylation of phenol with methanol in a mechanism different from that shown in figure 2-20 (Marczewski

et al., 1988). This mechanism, over H-Y but not over H-ZSM-5, is due to the anisole undergoing transalkylation with phenol. This is inhibited by size restrictions to the formation of the bulky bicyclic intermediate when occurring within H-ZSM-5. In this case only internal anisole rearrangement as a single molecule is being proposed, as it should not be prevented in a narrow zeolite pore such as that of H-ZSM-5.

It was observed that in phenol methylation over H-USY, the *o*- / *p*-ratio increased as conversion decreased with time-on-stream. Since this cannot be a classical product selective effect, given the size of the pores of zeolite Y, it is suggested that this is due to *p*-cresol being partly formed in a secondary reaction, probably as a result of phenol methylation with anisole (Parton *et al.*, 1989). It is likely that this would be prevented over H-ZSM-5.

Other researchers initially make suggestions of an anisole intermediate mechanism in the formation of *p*-cresol over zeolite H-Y, but go on to conclude that this was in fact not the case (Namba *et al.*, 1980).

2.8.6 Mechanism of *m*-cresol alkylation over γ -alumina

It has been shown that the mechanism of the reaction of methanol with phenol differs depending on whether the reaction is conducted over Brønsted or Lewis acid sites (Santacesaria *et al.*, 1990a).

Over a catalyst exhibiting strong Lewis acid properties (such as γ -alumina) phenol is attracted to the catalyst surface, binds with the oxygen and assumes a vertical orientation. The location of a Lewis acid site beside a basic site is crucial to this mechanism. A phenol molecule will interact with both the Lewis acid site and the Lewis basic site resulting in the vertical adsorption of a phenolate anion onto the acid site, and a hydrogen cation onto the basic site. Available hydrogen ions are assumed to be active enough to activate the methanol, and / or any other group present (Santacesaria *et al.*, 1990a).

Figure 2-21 shows an adapted version of this mechanism to illustrate the potential alkylation of *m*-cresol in the *ortho* position or onto the oxygen atom (3-methylanisole formation) (Santacesaria *et al.*, 1990a).

Santacesaria *et al.* (1990a) reported that γ -alumina was very *ortho* selective. For phenol methylation with methanol at reaction temperatures of 250 - 300°C *o*-cresol and 2,6-xyleneol were the main alkylated products. At a reaction temperature of 400°C some *m*-cresol (yield of between 23 and 30 mol %) and increasing amounts of xyleneols were produced. However at lower temperatures (200 - 230°C) anisole was the major product. It

was discovered that as the feed rate (and hence WHSV) was increased, the proportion of anisole within the product mixture increased. This was explained by the possibility that cresols are produced only partly by direct phenol alkylation with methanol and partly from anisole.

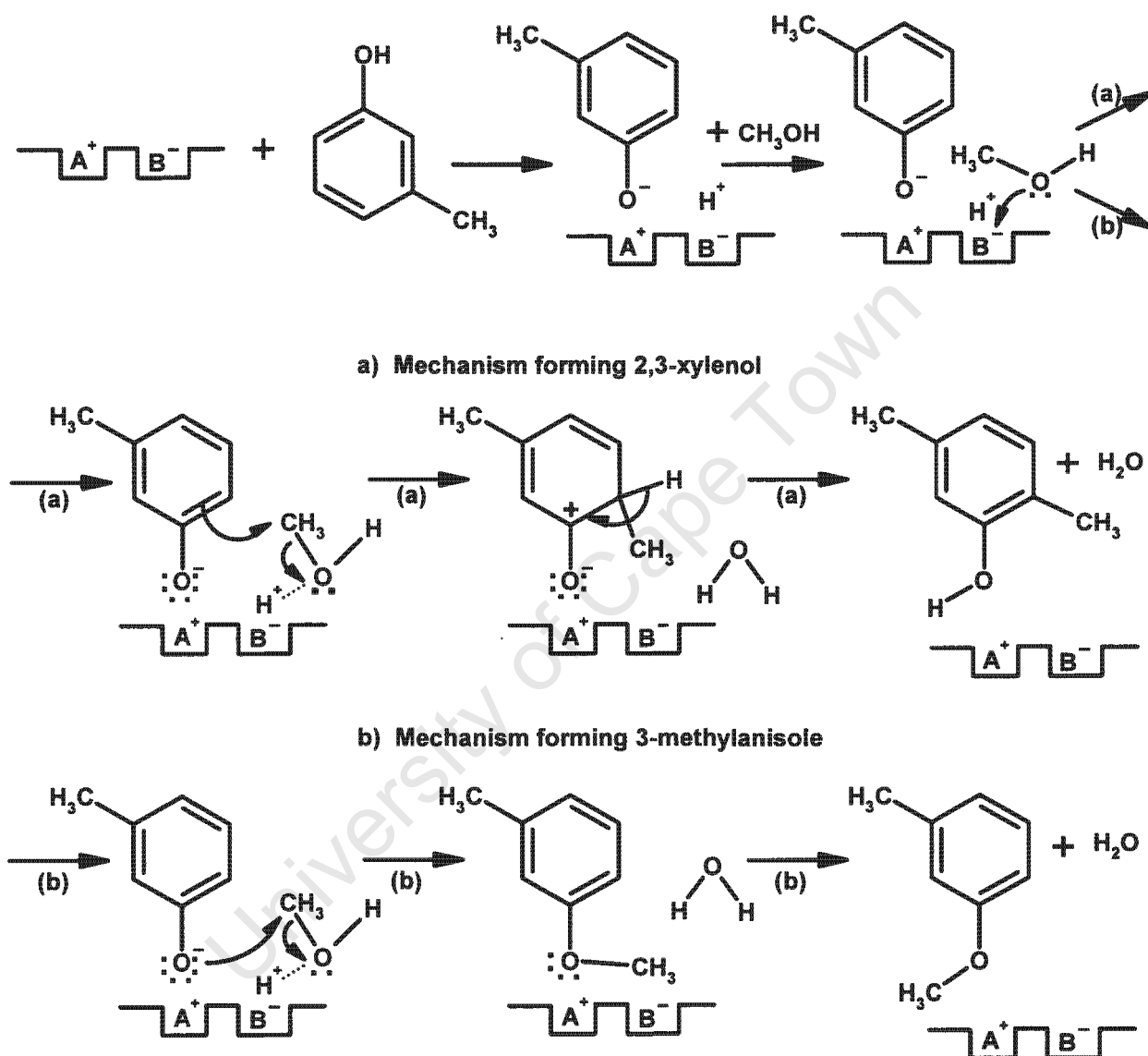


Figure 2-21: Mechanism of reaction of *m*-cresol and methanol on γ -alumina, where A^+ is a Lewis Acid site and B^- is a Lewis Basic site (adapted from Santacesaria *et al.*, 1990a)

Further experiments were conducted in attempt to establish whether anisole reacts via a bimolecular mechanism (i.e. transalkylation to form a phenol molecule and a methylanisole or cresol molecule) or via a monomolecular mechanism (anisole internal rearrangement to form cresol). It was suggested that at low temperature (200°C) the bimolecular reaction was dominant as relatively high amounts of phenol were found in the product mixture for the reaction of pure anisole over γ -alumina. As the temperature was increased (to 300°C) and space velocity increased, the proportion of *o*-cresol increased, thus suggesting that

the intramolecular rearrangement mechanism may be more prevalent as reaction temperature is increased (Santacesaria *et al.*, 1990a). However, for reaction over γ -alumina the active sites are not constrained by pores, which may restrict the bimolecular reaction. Thus it is possible, for reaction within narrow zeolite channels, that the intramolecular rearrangement mechanism is more dominant.

2.8.7 Mechanism of *m*-cresol ring alkylation over silica-alumina

A different reaction mechanism can be expected over silica-alumina as essentially Brønsted acid sites are present. Results from phenol methylation experiments conducted at 300°C show that both anisole and cresols were formed, thus indicating that alkylation occurs both on the oxygen atom and on the benzene ring. The reaction mechanism on a Brønsted acid site (such as that on silica-alumina) is slightly different from the reaction mechanism on a Lewis acid / base pair. It is evident that Brønsted acid sites interact strongly with the aromatic ring. Thus the phenol adsorption is never vertical as in the case of the phenolate anion. Thus, it is suggested that this reaction is not as selective to the *ortho* position but also to the *para* position, while coke is more easily formed (Santacesaria *et al.*, 1990a). Figure 2-22 shows the adapted reaction mechanism for methylation of *m*-cresol over Brønsted acid sites.

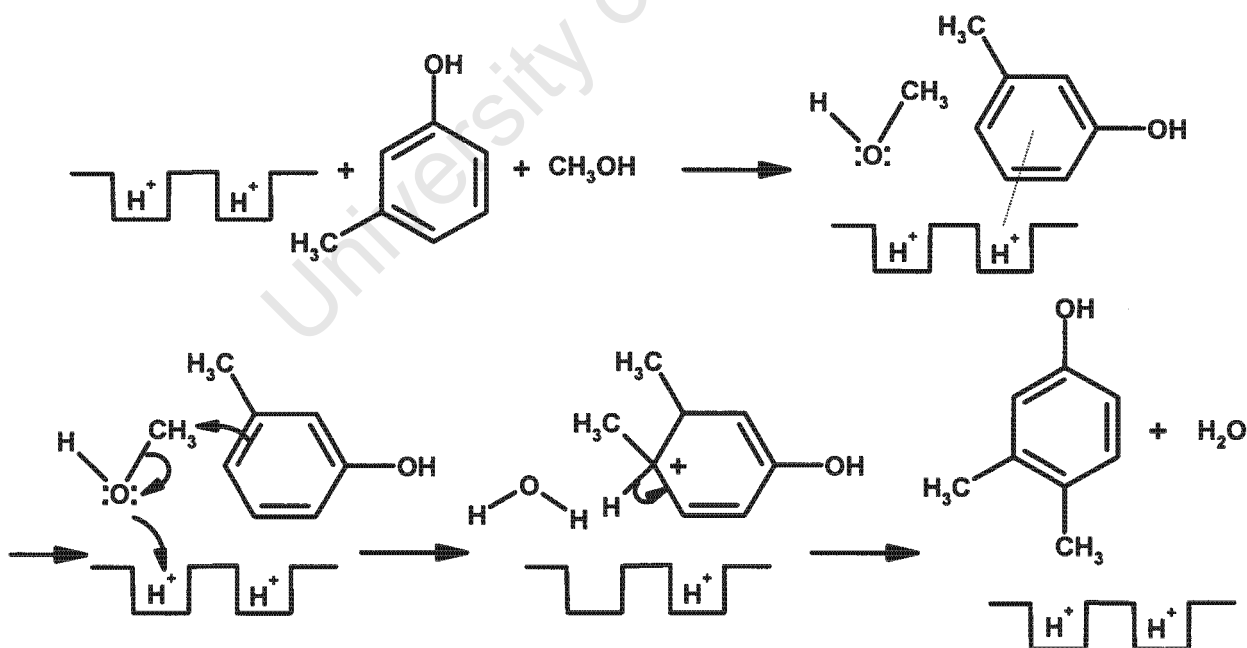


Figure 2-22: Mechanism of reaction of *m*-cresol and methanol to 3,4-xlenol on silica-alumina, where H^+ is a Brønsted acid site (adapted from Santacesaria *et al.*, 1990a)

2.8.8 Temperature effect on the mechanism of phenols alkylation

Santacesaria *et al.* (1990b) report apparent activation energies for the reaction of phenol with methanol and for the reaction of anisole as a sole reagent over H-ZSM-5 (refer to table 2-13 in section 2.6.2). These activation energies are related to overall phenol conversion, anisole production and ring alkylated product formation. For the reaction of phenol with methanol, lower activation energy is required to form anisole than "others". This indicates that anisole will be the preferred product at lower temperatures. For the reaction of anisole as a sole reagent, the activation energy required is higher than that for phenol methylation with methanol. This indicates that the conversion of anisole as a secondary reaction, i.e. in an isomerisation reaction that will probably occur as temperature increases; see section 2.8.5 (Santacesaria *et al.*, 1990b).

These findings indicate the 'O' alkylation is more prevalent at lower temperature while 'C' alkylation is more prevalent at higher temperature. This would be applicable to *m*-cresol methylation with methanol. At lower temperature selectivity to 3-methylanisole will be higher than selectivity to xlenol isomers. However, with increasing temperature selectivity to xlenol isomers will increase as selectivity to 3-methylanisole decreases.

2.8.9 Rideal kinetic mechanism

Santacesaria *et al.* (1990b) propose a Rideal kinetic mechanism for the reaction over H-ZSM-5. This is due to the isolated characteristics of the Brønsted acid sites in high silica zeolites (as in H-ZSM-5). Initially the methanol is adsorbed onto a free catalytic site (H-Z);



Then two competitive reactions could be proposed as alkylation to the oxygen and to the ring, respectively, where R-OH is an aromatic ring, substituted by a hydroxyl (Santacesaria *et al.*, 1990b);



(Santacesaria's mechanism has been modified slightly by replacing σ for the catalytic site by H-Z and $\text{H}^+ \text{Z}^-$ for the active (acid) site in a H-zeolite).

2.8.10 Possible side reactions

2.8.10.1 Over-alkylation, leading to the formation of multi-methylated products

Increasing the ratio of methanol : *m*-cresol in the feed can lead to increased methylation, which can result in the formation of increased amounts of tri- and tetra-methylated molecules. This could be valuable in cases where increased selectivity of higher methylated phenolics is required, but this is usually not desired.

In reactions where anisoles are formed, di- and tri-methylanisoles may be produced.

2.8.10.2 Decomposition of Methanol

Decomposition of methanol, resulting in the formation of H₂, CO, CH₄ and CO₂ may occur, but mainly over Fe containing catalysts as applied for the selective synthesis of *o*-cresol and 2,6-xyleneol (Fiege, 2003). The purpose of using Fe containing catalysts is mainly to balance the exothermic alkylation reaction with the endothermic methanol decomposition reaction, resulting in a cheaper reactor and simpler operation, however, higher feed cost (Böhringer, 2004).

It has also been reported that methanol, when passed over zeolites, is very reactive, producing low olefins, which also react with phenol, producing higher aromatic compounds as by-products of the phenols methylation (Chang *et al.*, 1989).

Balsama *et al.* (1984) investigated the conversion of methanol over various zeolites. They found that, for a feed of pure methanol at 250°C, over H-ZSM-5 65 % of methanol was converted to hydrocarbons (the hydrocarbon species are not reported), while over H-Y, 58 % of methanol was converted.

It was also reported that methanol conversion to dimethylether of 10 % was observed over H-ZSM-5 for methanol : phenol feed molar ratio of 1 : 2, reaction temperature of 300°C in vapour phase at atmospheric pressure (Landau *et al.*, 1997).

2.8.10.3 Isomerisation and transalkylation (at high temperatures)

At increasing temperature isomerisation is more likely to occur, yielding products closer to the thermodynamic equilibrium distribution. Thus, at higher reaction temperatures the proportion of xyleneol isomers created from primary *m*-cresol methylation products via secondary isomerisation reactions, such as 2,4- and 2,6-xyleneol, is likely to increase. However, higher temperature also encourages other secondary reactions which may be less desirable.

Over an acid catalyst, methyl groups migrate around the ring via an intramolecular 1,2-alkyl shift mechanism. In comparison, larger alkyl groups like ethyl, propyl etc. over large pore zeolites appeared to isomerise via intermolecular transalkylation. Researchers have found that over zeolite H-Y (a large pore zeolite) a significant proportion of isomerisation takes place via the bimolecular transalkylation mechanism. H-ZSM-5, with intermediate size pores, has shown shape selective properties in limiting transalkylation reactions while enhancing isomerisation (Imbert *et al.*, 2000).

In cresol isomerisation experiments it was noticed that there was a small degree of disproportionation (although practically negligible over H-ZSM-5, due to small size of the 10 member-ring zeolite not being conducive to disproportionation). Nevertheless, some disproportionation did occur. For reactant *p*-cresol the main disproportionation product expected was 2,4-xylenol. In practice, both 2,4- and 2,5-xylenol isomers were present, thus indicating isomerisation of 2,4-xylenol to 2,5-xylenol, which then desorbed rapidly (due to its slimmer structure). For reactant *m*-cresol, all the expected isomers, 2,5-, 3,4- and 2,3-xylenol, were present (for conversion of 10.6 %), but as conversion increased these isomers began to disappear as 2,4-xylenol began appearing (Imbert *et al.*, 1997). This indicates a driving force towards thermodynamic distribution as the thermodynamically preferred isomer, 2,4-xylenol is formed with higher selectivity at higher conversions. In *p*- and *m*-cresol isomerisation experiments over H-Y, transalkylation products were formed at rather high selectivity, of between 20 % and 34 % (Imbert *et al.*, 2001).

2.8.10.4 Other products observed

Literature reports a variety of other products that are present in the methylation products of phenol and cresol. The selectivities of these by-products are dependent on operating conditions. Substances that have been observed in the product streams besides anisole, cresols and xylenols, include trimethylphenols, methylanisoles, dimethylanisoles and trimethylanisoles (Balsama *et al.*, 1984, Landau *et al.*, 2001 and Santacesaria *et al.*, 1990a & b).

The formation of diphenylether from phenol has also been reported (Chantal *et al.*, 1985).

2.9 Effect of zeolite properties

2.9.1 Catalyst acidity and the effect of varying SiO₂ / Al₂O₃ ratio

SiO₂ / Al₂O₃ ratio affects the specific acidity, as catalysts with lower ratios have a higher number of acid sites. In the introduction to section 2.8 and in section 2.8.9 the effect of SiO₂ / Al₂O₃ ratio was introduced along with mechanistic discussions. Acid strength of individual sites increases with increasing SiO₂ / Al₂O₃ ratio (Flanigen, 1991). However, it has been reported that activities of zeolites H-ZSM-5 and H-Y, for the methylation of phenol with methanol, decreases with increasing SiO₂ / Al₂O₃ ratio (Landau *et al.*, 1997). This is due to the decreasing number of sites, outbalancing the increase in individual strength.

It has been reported that selective formation of *p*-cresol, as well as *p*-xylene (in the alkylation of toluene) is dependent on the strength of the Brønsted acid sites (to encourage 'C' alkylation) and on the narrow space of a zeolite channel to prevent formation of the *ortho* and *meta* isomers, which are slightly more bulky than the *para* isomer (see section 2.7.2.4.2).

Namba *et al.* (1984) investigated the effect of acid strength of H-Y zeolite in the alkylation of phenol with methanol. The results showed that weak acid sites produced higher proportions of anisole, while the strong acid sites initiated secondary alkylation to xylenols and some isomerisation of *p*-cresol to *m*-cresol. Thus it appears that over weaker acidic sites, 'O' alkylation is favoured while over stronger acidic sites, 'C' alkylation is favoured.

2.9.2 Zeolite crystal size

Experiments investigating the effect of the size of H-ZSM-5 crystals found a strong influence on *p*-selectivity (Olson and Haag, 1984). This is due to intracrystalline diffusion effects (product selectivity, see section 2.7.2.4.2). The crystal diameter (denoted in equation 2-1 by R, the crystal radius) affects the amount of material that can diffuse within the pore as it determines the pore length and is a factor that contributes to the Thiele Modulus with second power, as shown in equation 2-2 (Fogler, 1999).

Equation 2-2: Relationship between the Thiele Modulus and rate of reaction, the diffusivity constant and radius of particle (Fogler, 1999)

$$\varphi_n^2 = \frac{k_n \cdot C_{As}^{n-1} \cdot \rho_c \cdot S_e \cdot R^2}{D_e} \approx \frac{\text{reaction rate}}{\text{diffusion rate}}$$

In addition, smaller crystals have a higher proportion of unselective active sites on the external surface of the crystal itself.

Santacesaria *et al.* (1990b) showed that initial activities, over H-ZSM-5, are more sensitive to the crystalline diameter than to specific acidity. They were also able to conclude that intracrystalline diffusion over H-ZSM-5 affects phenol conversion rates even in cases where very small crystallites (0.022 – 0.028 Å) were used (Santacesaria *et al.*, 1990b).

2.9.3 Zeolite pore size

Investigation of cresol isomerisation over H-ZSM-5 found that the pore size favoured isomerisation rather than bimolecular reaction (where transalkylation occurred between two cresol molecules) (Imbert *et al.*, 1997), see also section 2.8.10.3. It was also reported that rates of conversion over H-ZSM-5 are dependent on the cresol isomer fed and decrease in the following order: *para*- >> *meta*- > *ortho*-, which can be explained by the product shape selectivity of the zeolite. *p*-Cresol has the smallest kinetic diameter thus allowing for a higher rate of diffusion within the zeolite channels.

In comparison, the kinetic diameters of water and methanol are small (<4Å). There will be no diffusion restrictions on these molecules within the channels of zeolite H-ZSM-5.

2.10 Effect of various reaction parameters on product distribution

Selection of appropriate reaction parameters is important in achieving the most desired product distribution. The effects of changing various parameters of phenols alkylation reactions have been investigated by many researchers. Following is a discussion of some reaction parameters and their effect on the reaction and product distribution.

2.10.1 Temperature

Temperature has a definite effect on the product distribution in the methylation of phenolics.

Reaction at higher temperatures favours the formation of carbon alkylates, while 'O' alkylation is preferred at lower temperatures (see section 2.8.5). Phenol methylation over various catalysts (γ -alumina, with strong Lewis acid sites, Nafion, with strong Brønsted acid sites, silica-alumina, with both Lewis and Brønsted sites and phosphoric acid supported on Kieselguhr, with Brønsted sites of medium and weak strength) showed that more cresols are formed with increasing temperature (Santacesaria *et al.*, 1990a).

At high reaction temperatures ($\sim 450^\circ\text{C}$) strongly acidic catalysts are very active but show little selectivity.

Santacesaria *et al.* (1990a) investigated the effect of reaction temperature for the methylation of phenol with methanol over γ -alumina and silica-alumina. At low temperature (200°C) selectivity to anisole was highest for phenol conversion of 2.5 %. As the reaction temperature was increased the conversion of phenol increased to 4.9 % at 250°C and then to 8.7 % at 300°C and some 2,6-xilenol was produced (see figure 2-23). In comparison to reactions over γ -alumina and silica-alumina, lower selectivity to anisole was observed over γ -alumina at slightly higher conversion and similar reaction temperatures. In conclusion it was found that temperature had the most significant effect on selectivity. Note that the comparison by Santacesaria *et al.* (1990a) was done at different conversions.

However, different investigations showed that anisole formation has indeed a lower activation energy than cresol formation, at least over γ -alumina (Tleimat-Manzalji *et al.*, 1993 and Santacesaria *et al.*, 1990b), see tables 2-12 and 2-13.

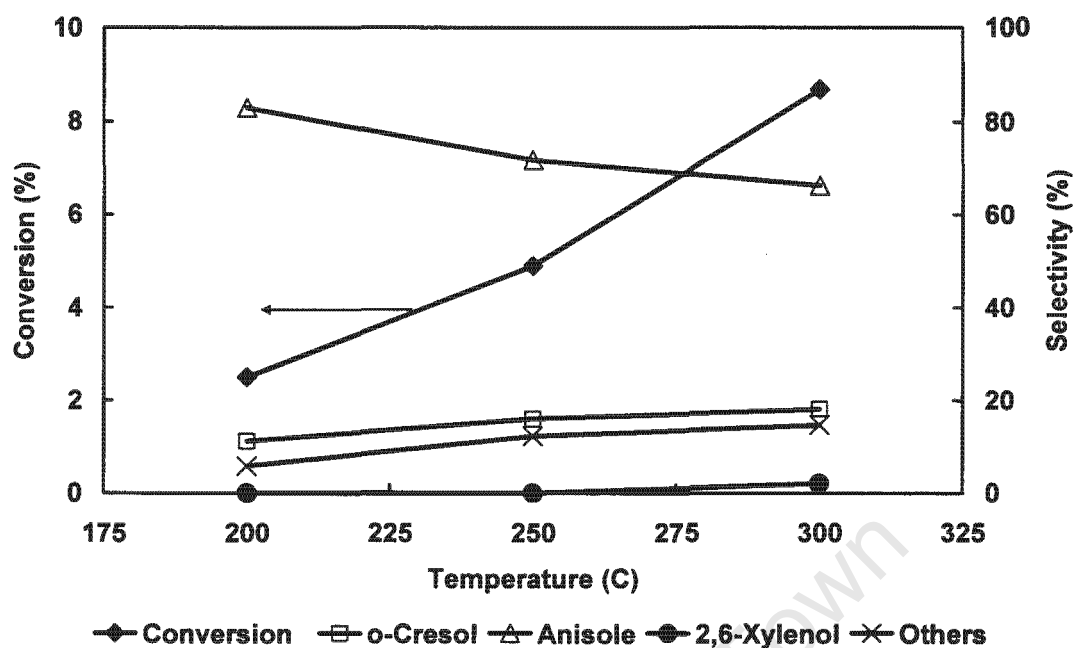


Figure 2-23: Change in product composition with increasing reaction temperature and conversion for phenol methylation with methanol (phenol : methanol molar feed ratio of 2:1) over silica-alumina at a space velocity of 15.6 ml / g · h (Santacesaria *et al.*, 1990a). Note that the major product is anisole.

Santacesaria *et al.* (1990a) reported similar results for reactions carried out over H-ZSM-5. Landau *et al.* (2001) conducted research into the methylation of phenol over zeolite H-Beta (figure 2-24). It is a little surprising that the conversion of phenol did not rise further as reaction temperature was increased from 300°C to 500°C. It was concluded that this was due to extensive deactivation of catalyst at 500°C due to interaction of water with active catalyst sites. Selectivity to *m*- and *p*-cresol increased with increasing reaction temperature while anisole selectivity declined (Landau *et al.*, 2001). However, the increase in *p*-selectivity may indicate increased diffusion constraints due to accelerated coking.

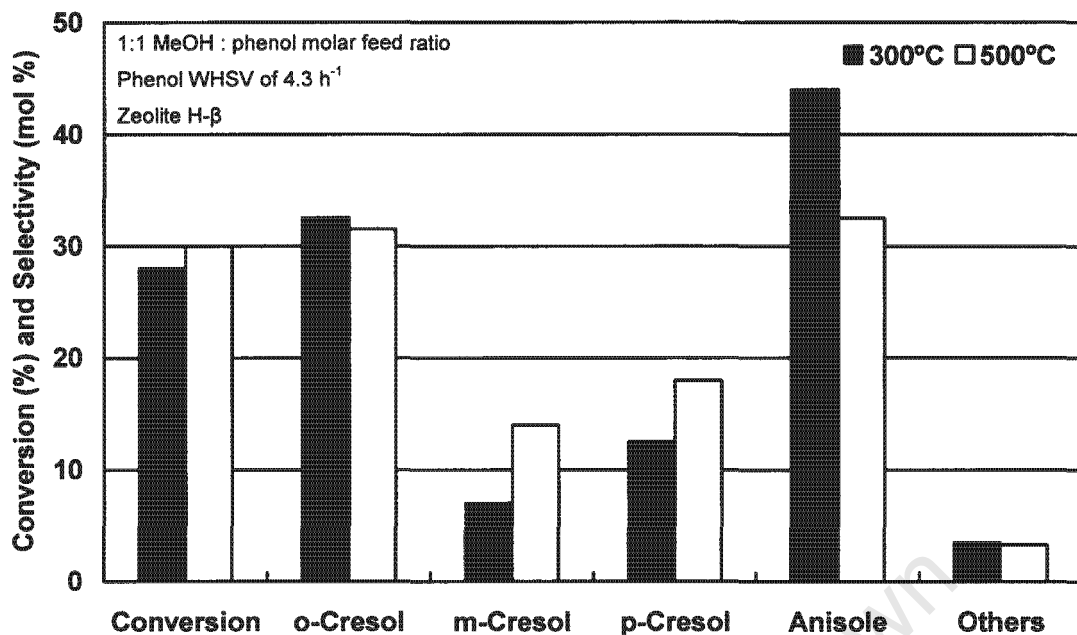


Figure 2-24: Conversion of methanol with phenol and selectivity to products over H-Beta (Landau *et al.*, 2001)

2.10.2 Pressure

Methylation of phenolics in vapour phase is usually carried out at low pressure, while trickle phase (or liquid phase) methylation is carried out at elevated pressure. The pressure is needed to keep the phenol and phenolic products in liquid phase. Liquid phase reactions are usually advantageous as catalyst deactivation rate is reduced. This is due to a “washing” effect, whereby heavy coke precursors dissolve in the reaction mixture and are removed from the catalyst, although more expensive equipment is required. It has been reported that similar product distributions are obtained for reactions in liquid and gaseous phase (Fiege, 2003).

In terms of le Chatelier's principle, in equilibrium there is no pressure effect since the number of moles doesn't change. In these methylation reactions there are 2 moles of reactants and 2 moles of product (including water), so that increasing pressure will not be able to push any methylation equilibrium one way or another. Note that pressure does have effect on accelerating rates and increasing conversion (O'Connor *et al.*, 2003).

However, it has been suggested that product distribution can be affected by pressure. Moon *et al.* (2004) conducted experiments to determine the effect of pressure in shape selective phenol methylation with methanol. Liquid phase batch experiments conducted over H-MCM-22 (small zeolite crystals of ~0.2 μm) at low reaction temperatures of 200 – 250°C, methanol : phenol molar feed ratio of 1 and autogeneous reaction pressures of 23

– 41.5 bar produced high p : o -cresol ratios of 1.2 – 1.3. Experiments conducted at low feed partial pressure of 0.2 bar, in gas phase, produced lower p : o cresol ratios of 0.5, which corresponds to the statistical ratio. This phenomenon was attributed to the fact that high pressure may increase the occupancy of the pore system with phenol, thereby increasing the effective diffusional constraints. The increase in diffusional constraints would then increase the effect of product shape selectivity (i.e. preference for the 'slimmest' product isomer) towards p -cresol. Note that in similar experiments that were conducted over H-ZSM-5 crystals of ca. 14 μm this phenomenon was not observed (Gama *et al.*, 2003). This was attributed to the fact that H-MCM-22 has slightly smaller pores and fewer interconnecting pore channels than H-ZSM-5 and thus will force increased diffusional constraints on the product, when compared with H-ZSM-5 (Moon *et al.*, 2004).

Other researchers have reported that, in the case of propylation of m -cresol with propene over H-ZSM-5, reaction pressure had an indirect effect on the selectivity, namely via conversion (O'Connor *et al.*, 2003).

2.10.3 Space velocity (contact time)

It is known that space velocity has an impact on the performance of catalytic reactions. Decreasing space velocity (i.e. increasing the residence time) increases the period that the reactant spends in contact with the catalyst. This provides a greater opportunity for a reaction to occur. Thus it is normally true that with decreasing space velocity conversion increases. With increase in conversion the occurrence of secondary and even tertiary reactions becomes more likely. Thus, by manipulating the space velocity, secondary and tertiary reactions can be encouraged or discouraged and the overall product distribution can be altered.

Typical LSHV used in industry for phenol alkylation over acid catalysts are between 0.5 and 2.0 h^{-1} (Fiege, 2003).

It is reported that, in the case of propylation of m -cresol with propene over H-ZSM-5, space velocity did not have any direct effect on product selectivity. The shape selective effects observed were indirect, i.e. via conversion (O'Connor *et al.*, 2003).

2.10.4 Mass of catalyst

By varying the amount of catalyst present within the reactor the space velocity (contact time) can also be manipulated. Ideally it is better to pack into a reactor as much catalyst as possible and vary contact time through manipulation of space velocity (or pump rate).

2.10.5 Methanol : *m*-cresol feed ratio

Typical methanol : phenol (or alkylation agent : phenolic compound) molar feed ratios used in industry are 1 – 4. Water is sometimes added to the feed to mitigate coking.

It has been reported that when the methanol : phenol molar feed ratio was decreased from 5 to 0.5 over H- β and H-Y there was little effect on product selectivity (Landau *et al.*, 2001).

However, increasing the methanol content in the feed above 1 : 1 increases the proportion of di- and tri- methylated phenolics, thus, in industry, the *o*-cresol : 2,6-xylenol ratio in *o*-selective phenol alkylation over basic catalysts is controlled through manipulation of the methanol : phenol feed ratio. Where only or mostly 2,6-xylenol product is desired, the ratio is rather high and *o*-cresol is recycled in the feed (Fiege, 2003).

The effect of methanol : phenol ratio was investigated over H-Y (Namba *et al.*, 1980). It was found that *p*-cresol yield was maximised at methanol : phenol molar feed ratio of 2. At higher molar feed ratios, yields of xylenol isomers increased while yields of *o*-cresol and anisole decreased. Also, at higher methanol : phenol molar feed ratios, the proportion of higher alkylated products increased.

By increasing methanol : phenol molar feed ratio from 1 : 1 to 5 : 1 over H-Y it was observed that more methanol was consumed in side reactions while more anisole and less *o*- and *p*-cresols were formed (Balsama *et al.*, 1984).

In phenol methylation reaction over alumina it was found that the production of dimethylether increased as feed content of methanol increased, and *vice versa* (Tleimat-Manzalji *et al.*, 1993).

2.10.6 Catalyst stability / deactivation with time-on-stream

Santacesaria *et al.* (1990a) found deactivation of γ -alumina between 200 – 300°C to be negligible and very low at 400°C. However, in comparison, it was observed that silica-alumina deactivates at a much quicker rate. This was attributed to the coking on the Lewis acid sites.

In phenol methylation over H-ZSM-5, catalyst deactivation occurred throughout the duration of the experiment. It was observed that during the first 50 hours of reaction the conversion dropped from initially 17 % to 11 %. A small, but not negligible shift in product distribution was observed during this period as the selectivity to anisole increased slightly, from around 55 % to 64 %, while the selectivity to cresols dropped correspondingly (figure 2-25). The total phenomenon was attributed to poisoning of external acidic sites

(Santacesaria *et al.*, 1990b). As the proportion of external acidic sites falls in relation to internal acidic sites, it would be expected that product shape selectivity would increase. In addition, secondary or higher reactions would also have a greater chance of occurring.

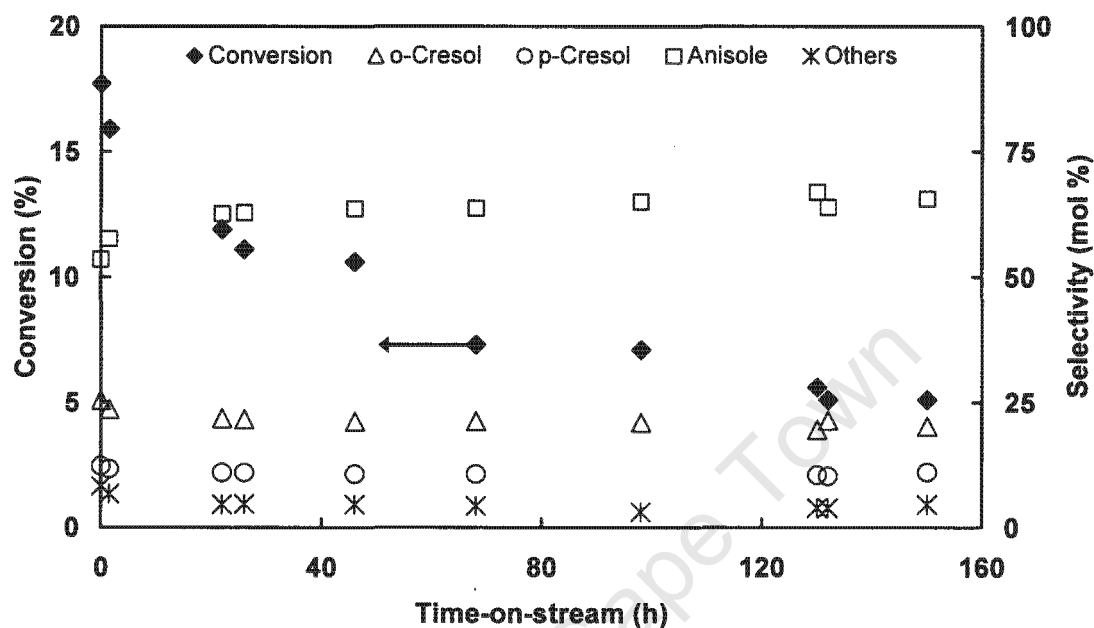


Figure 2-25: Decline of conversion and change in selectivity with H-ZSM-5 catalyst deactivation with time-on-stream for methylation of phenol with methanol at 300°C, feed rate of 13.3 g_{phenol} / g_{active catalyst} · h and phenol : methanol molar feed ratio of 2 : 1 (Santacesaria *et al.*, 1990b)

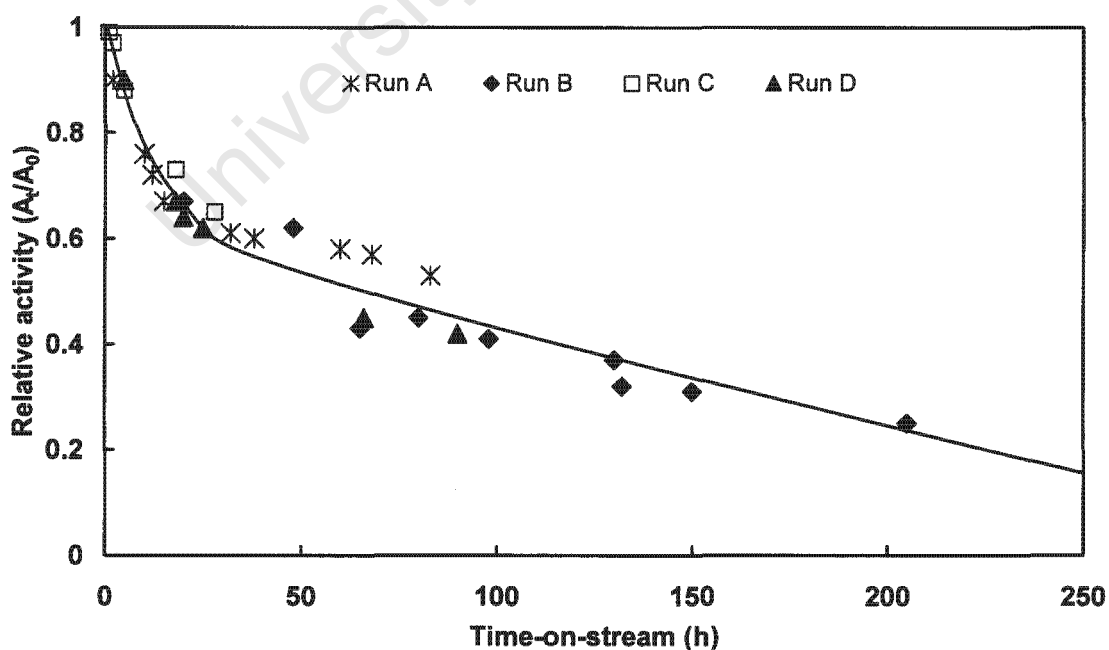


Figure 2-26: Change in relative activity of H-ZSM-5 for at reaction temperature of 260 - 350°C, various feed rates and various feed ratios of phenol, methanol and anisole. Runs A and B were performed with 1 g zeolite, run C with 2 g and run D with 3 g zeolite (Santacesaria *et al.*, 1990b)

Figure 2-26 shows the relative activity of H-ZSM-5 for 250 hours. In these experiments normally phenol and methanol comprised the reactant feed mixture, but in some cases anisole alone, or phenol and anisole together were fed as reagents. Four different campaigns are portrayed and for each campaign the trends are similar. Following the relatively quicker deactivation during the initial 50 hours, catalyst deactivation reflects a linear relationship over the subsequent 200 hours. It was reported that after the initial deactivation (over 50 hours) the product distribution was not significantly affected by further catalyst deactivation. It was concluded that pore constraints did not change appreciably during this period. The reason given is that catalyst deactivation during this period (between 50 and 250 hours on stream) excluded the deposition of coke within the zeolite cavities (Santacesaria *et al.*, 1990b). Had the zeolite cavities experienced coke deposition the product distribution would have changed.

The slow deactivation between 50 and 250 hours on-stream, is explained through increase in resistance to pore diffusion, originating from coke deposition within proximity of the zeolite pore entrances (Santacesaria *et al.*, 1990b). However, the *ortho* / *para* ratio remained constant at 2 (for reaction temperature of 300°C) during the period of linear deactivation indicating that a pore entrance narrowing or blocking effect through coke deposition probably did not occur.

It was noticed that as γ -alumina deactivated at high reaction temperature of 400°C, the distribution of cresol product changed (figure 2-27). More *o*-cresol was produced at the expense of *m*-cresol (i.e. the catalyst became more selective to *ortho* alkylation). It was suggested that this is due to *m*-cresol being produced on the stronger acid sites and as the catalyst deactivates, selectivity to *m*-cresol decreases (Santacesaria *et al.*, 1990a). However, when regarding *m*-cresol as a secondary product formed through isomerisation (at least in part) this phenomenon could simply be seen as a deviation from the initially established thermodynamically controlled distribution of cresols when the catalyst deactivates and conversion declines.

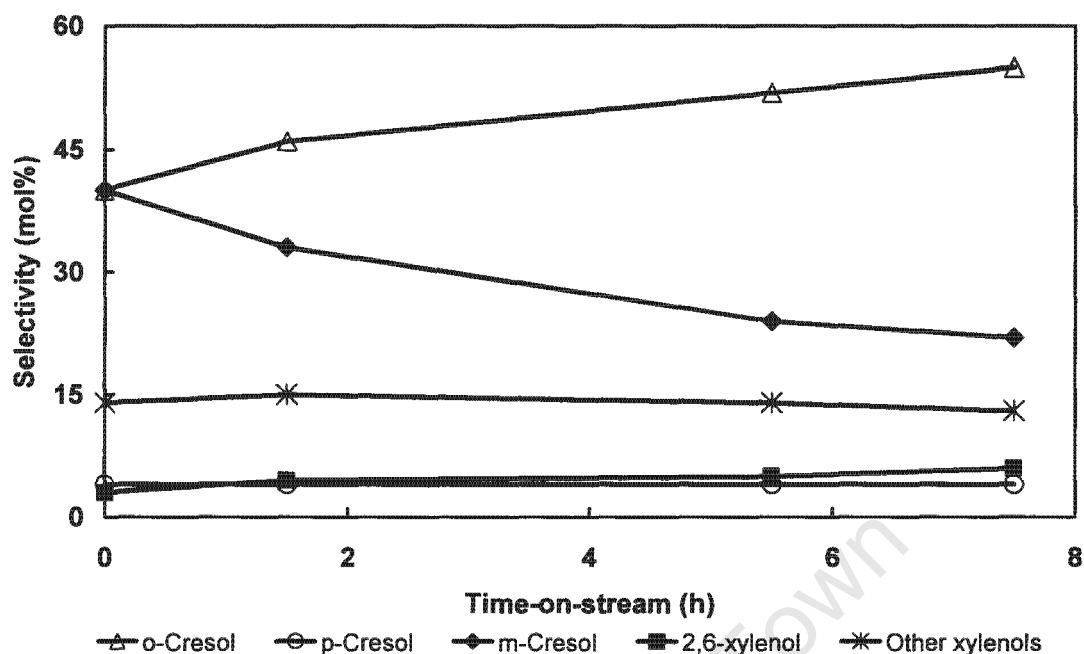


Figure 2-27: Change in selectivity to cresol isomers and others with deactivation of γ -alumina for phenol methylation with methanol at 400°C (Santacesaria *et al.*, 1990a). Within the duration of this experiment relative activity dropped to ~85 % over 7.5 hours. The change in conversion is not reported.

It has been observed that in the alkylation of anisole with methanol over zeolite catalysts, conversion also decreased with time (probably due to deposition of coke). These experiments were carried out in vapour phase at 200°C over H-ZSM-5, H-ZSM-11 and H-USY (2 types with different $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratios) (Parton *et al.*, 1989).

In the alkylation of phenol with methanol over the pentasil zeolites, it was found that the *o*-/*p*- ratio decreased with time-on-stream. This was explained by the build up of coke deposits, which decrease the effective pore size either by a pore-mouth blocking mechanism or by homogeneous deposition throughout the crystal (Parton *et al.*, 1989).

It is more likely that the effect of coking results in pore or pore mouth blocking, i.e. longer diffusion pathways rather than “decreased pore size” (O’Connor *et al.*, 2002).

3. Objectives of this Study and Hypothesis

3.1 Objective

The objective of this research was to evaluate the opportunity for the shape selective methylation of *m*-cresol with methanol over potentially shape-selective zeolites i.e. for the preferential formation of the slimmest xylene product or products.

With the decline in cresols and xylenols production via isolation from coal tars and spent refinery caustics and with the difficulty and high cost of separating certain cresol and xylene isomer mixtures, the development of processes in which particular cresol and xylene isomers can be produced at increased selectivity, is very attractive.

3.2 Xylene products expected from methylation of *m*-cresol

In the reaction of methanol and *m*-cresol (barring any pre-isomerisation of the latter) there are only four positions on which the methyl group can attach to the cresol ring (the two *ortho*, the second *meta* and the *para* position). Thus the primary products expected are the 2,3-, 2,5-, 3,4- and 3,5- xylene isomers. The two other xylene isomers (2,4- and 2,6-xylene) can only be produced via a second reaction, namely an additional 1,2-shift of the existing methyl group. These reaction pathways are shown in figure 3-1. Since the *o*- and *p*-positions on the ring of a phenol molecule are far more reactive than the *m*-position, 2,5-xylene, 2,4-xylene and 2,3-xylene were expected to form with preference.

When the reaction takes place in the confines of a narrow zeolite channel, shape-selectivity in the form of product selectivity can be expected to occur. Of the primary products, 2,5-xylene was expected to be the most prevalent product under such confines as it is the slimmest isomer with the comparably bulky methyl groups in *para*-position with respect to each other. Thus 2,5-xylene would diffuse out of the zeolite channels with greater ease than any of the other xylene isomers, which would then isomerise internally to the 2,5-xylene isomer.

3,4-Xylene was also expected to form with some preference, although to a smaller extent than 2,5-xylene since 3,4-xylene is a slightly more bulky molecule with its methyl groups in *ortho*-position to each other and the hydroxyl group opposite of them.

Formation of 2,3-xylene was expected to be somewhat suppressed as methyl group attachment onto the 2-position would experience some sterical hindrance (due to the

hydroxyl group in the one adjacent position and the methyl group in the other). Also, 2,3-xlenol is slightly more bulky a molecule than 2,5-xlenol, with its methyl groups in *ortho*-position to each other and the hydroxyl group next to it.

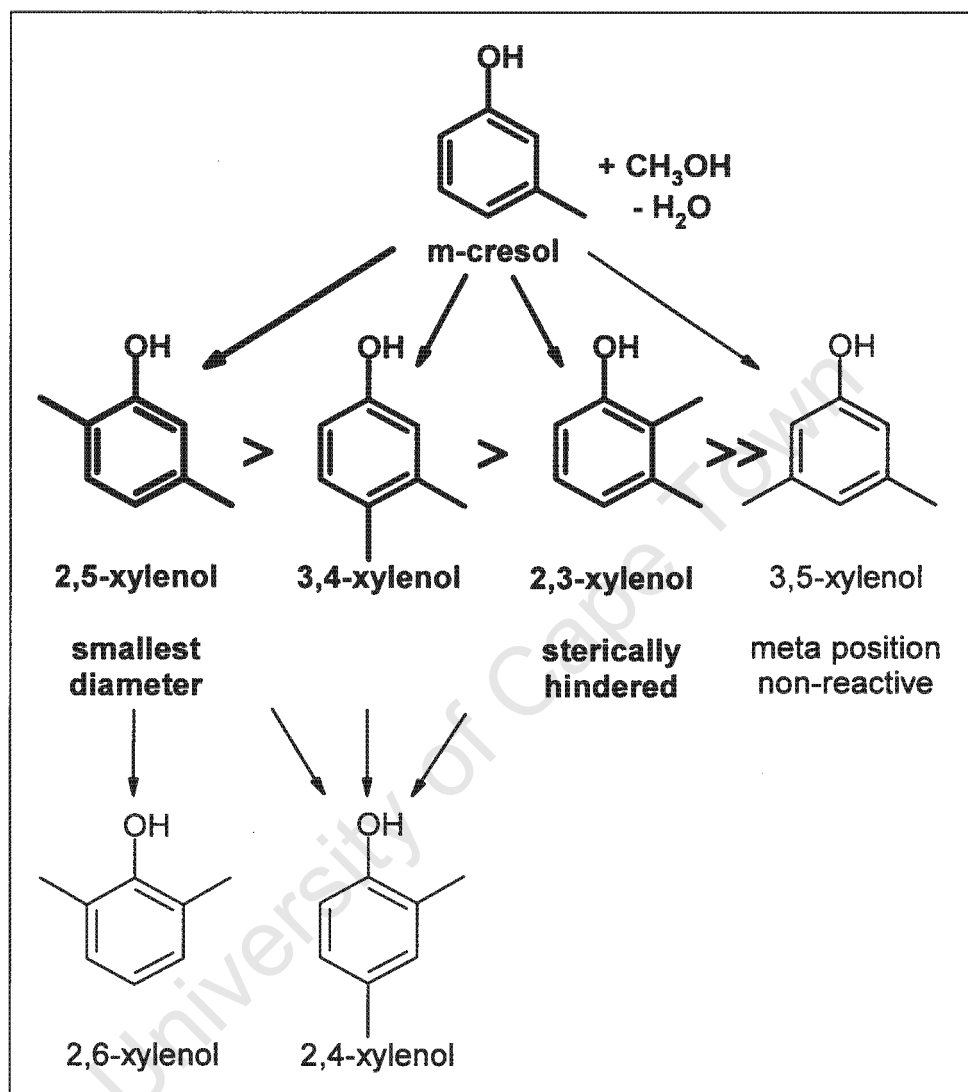


Figure 3-1: Primary (top) and secondary (bottom) reaction pathways of *m*-cresol methylation with methanol over acid catalysts as well as kinetically favoured (bold) and non-favoured products (not in bold)

3,5-Xlenol formation was expected to be suppressed as the *meta*-position is less reactive than either *ortho*- or *para*-positions.

Small amounts of 2,4- and 2,6-xlenol may be present due to secondary reactions. There are two reaction pathways that can lead to the formation of 2,4- and 2,6-xlenol. Firstly, isomerisation can occur on the primary methylation product, i.e. after the addition of the second methyl group (as shown in figure 3-1). Secondly, prior to methylation, *m*-cresol can initially undergo isomerisation where the methyl group moves from the *meta*-position

to either a *para*- or *ortho*-position. Subsequently, when methylation occurs in the *ortho*-position, either 2,4- or 2,6-xylenol may be formed.

Thus under kinetic control, 2,5-xylenol would be expected as the most abundant molecule. More 3,4-xylenol is expected than either 2,3- or 3,5-xylenol, while only small amounts of 2,4- and 2,6-xylenol may be present, particularly at low conversion.

3.3 Hypothesis

Application of commercially available, potentially shape-selective zeolites can improve the selectivity (to a commercially interesting level) of the most linear xylenol isomers produced from *m*-cresol by methylation with methanol.

3.4 Key questions

The following key questions were to be answered:

1. Are commercially available acid zeolite catalysts active for *m*-cresol methylation to xylenols?
2. Is stable operation possible?
3. What is the shape-selectively favoured xylenol isomer?
4. To what extent do commercially available, potentially shape-selective, acid zeolites with typically small crystal size effect a shape-selective product?
5. Which is the preferred zeolite for shape-selective *m*-cresol methylation to the shape-selectively favoured xylenol isomers?
6. How does the product distribution, in particular the xylenol isomer distribution, as obtained over the potentially shape-selective acid zeolites, compare with that produced over a non-shape-selective catalyst?
7. What influence do operating conditions (temperature, pressure, space velocity and methanol : *m*-cresol feed ratio) have in respect of conversion and selectivity?

4. Experimental

Five potentially shape-selective acid zeolites and one non-shape-selective catalyst were tested in this study. All of the catalysts tested were supplied by industrial catalyst manufacturers, are regular products and are commercially available. The reactants used in this study, *m*-cresol and methanol, were of commercially available quality and were used without further purification.

4.1 Catalysts

All catalysts tested were in their acidic form. Catalysts in both extrudates and zeolite crystal powder form were tested. Where extrudates were tested, binder weight of 20 weight % was assumed (Fletcher, 2002). This was taken into account when calculating WHSV. Inert SiC, particle size of $\leq 930\text{ }\mu\text{m}$, was used for dilution of the catalyst bed at a ratio of 1:1 on a volume basis. The zeolites tested were typical commercial materials with crystal sizes that can be assumed to be of around 0.1 to 0.2 μm (Fletcher, 2002).

The properties of the different zeolites are given in table 4-1. Two medium pore size zeolites, FER and MFI were tested. For MFI samples, zeolites of two different $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratios were applied. Two wide pore zeolites, MTW and BEA, were included. For comparison, MOR with a unidimensional pore structure was also tested. In order to compare for shape-selective effects, non-shape-selective amorphous silica-alumina (Siral-40) was also tested.

Table 4-1: Catalysts tested

Sample code	Type material	Catalyst form	Size	Manufacturer	SiO ₂ / Al ₂ O ₃ molar ratio*	Ring**	Channel size*** (Å)
FER-20	H-Ferrierite	Extrudates	1/16"	Zeolyst	20	10	4.2 x 5.4
MFI-90	H-ZSM-5	Extrudates	1/16"	Süd-Chemie	90	10	5.3 x 5.6
MFI-220	H-ZSM-5	Extrudates	1/10"	Süd-Chemie	220		5.1 x 5.5
MTW-100	H-ZSM-12	Extrudates	1/16"	Süd-Chemie	100	12	5.6 x 6.0
MOR-90	H-Mordenite	Extrudates	1/16"	Zeolyst	90	12	6.5 x 7.0
BEA-150	H-Beta	Zeolite crystal powder	-	Syncat	150	12	5.6 x 5.6 6.7 x 6.6
Siral-40	Amorphous silica-alumina	Powder	-	Sasol-Germany (formerly Condea)	1.13****	Amorphous	Amorphous

* Manufacturer's data, the number also appears in the sample code of the zeolites

** Number of T-atoms (Si + Al) forming channel opening, 8-membered ring channels ignored

*** From IZA website (IZA, 2004), 8-membered ring channels ignored

**** Siral-40 comprises 60 wt % Al₂O₃ and 40 wt % SiO₂, which is equivalent to 47 mol % and 53 mol % respectively. Hence 53 / 47 is equivalent to SiO₂ / Al₂O₃ molar ratio of 1.13 (Sasol, 2005)

4.2 Feed stocks

m-Cresol

m-Cresol, with purity of >99 %, was obtained from Riedel-de Haën.

Methanol

Methanol, of HPLC grade (>99.9 % pure), was obtained from Sigma-Aldrich.

Nitrogen

Nitrogen, of purity >99.999 %, was obtained in cylinders, at 200 bar, from Messer Fedgas.

Synthetic Air

Synthetic air, of purity >99.999 % was obtained in cylinders, at 200 bar, from Messer Fedgas.

Impurities in Feed Components

The *m*-cresol used was injected into a Gas Chromatograph (GC) (see section 4.5) to check for impurities. GC analyses showed that the *m*-cresol indeed contained small amounts (approximately 0.7 mol %) of impurities, mainly *p*-cresol (see table 4-2). This was taken into account when calculating conversion and selectivity. Methanol did not contain detectable amounts of organic impurities.

Table 4-2: Impurities in feed component *m*-cresol

Component	Abundance (mol %)
<i>m</i> -Cresol	99.3
<i>p</i> -Cresol	0.6
Others	0.1*
Total	100.0

*Evaluated as cresols

4.3 Catalyst performance testing apparatus

A schematic of the experimental apparatus, as used in this work, is shown in figure 4-1. All parts were made from stainless steel, SS 316. Gas feeding facilities (for nitrogen and synthetic air) were used to dry and activate the catalyst, to inertise the experimental apparatus and to control the reaction pressure. Note that during the experiments only

liquid mixtures of methanol and *m*-cresol were fed into the reactor, i.e. no carrier gas was used in any of the experiments.

4.3.1 Nitrogen and synthetic air feed

Gaseous nitrogen and synthetic air were supplied from cylinders. The flow rates were controlled by a 20 cm³ / min rated Mass Flow Controller (MFC). A filter (located before the Mass Flow Controller) was used to protect the Mass Flow Controller from any solids possibly entrained in the gas stream. A check valve and a 500 ml guard catch pot (both located after the Mass Flow Controller) were installed to protect the Mass Flow Controller from any liquid back flow from the reactor in case of downstream blockages or erroneous operation. The Mass Flow Controller calibrating procedure is detailed in appendix 3.

N₂ and synthetic air (for catalyst drying and activation) were fed into the reactor casing near the bottom. (This gas inlet was originally designed for experiments using a carrier gas. The carrier gas would also have also prevented any liquid feed from trickling over the lip of the reactor tube and being lost from the reaction. However, this application was not used in any of the experiments conducted.)

4.3.2 Liquid feed

An HPLC metering pump (HP 1100; flow range of 0.01 – 5 ml / min, adjustable in steps of 0.01 ml / min) supplied the liquid feed mixture to the top of the evaporator / preheater section of the reactor (for details see figure 4-2). The liquid feed pot was situated on a balance to check pump rates. The liquid feed passed over the tip of a fixed thermocouple immediately after introduction to the evaporator / preheater zone of the reactor to measure the temperature of the feed before it dispersed over the silicon carbide (SiC) packing in the evaporator / preheater. This thermocouple was used to ensure that the liquid feed temperature at the entrance to the evaporator was below the boiling point of the feed mixture at the given reaction pressure to ensure that no premature or other irregular evaporation occurred in the feed line with possible consequence of pulsating feed flow and inconsistent space velocity and feed composition.

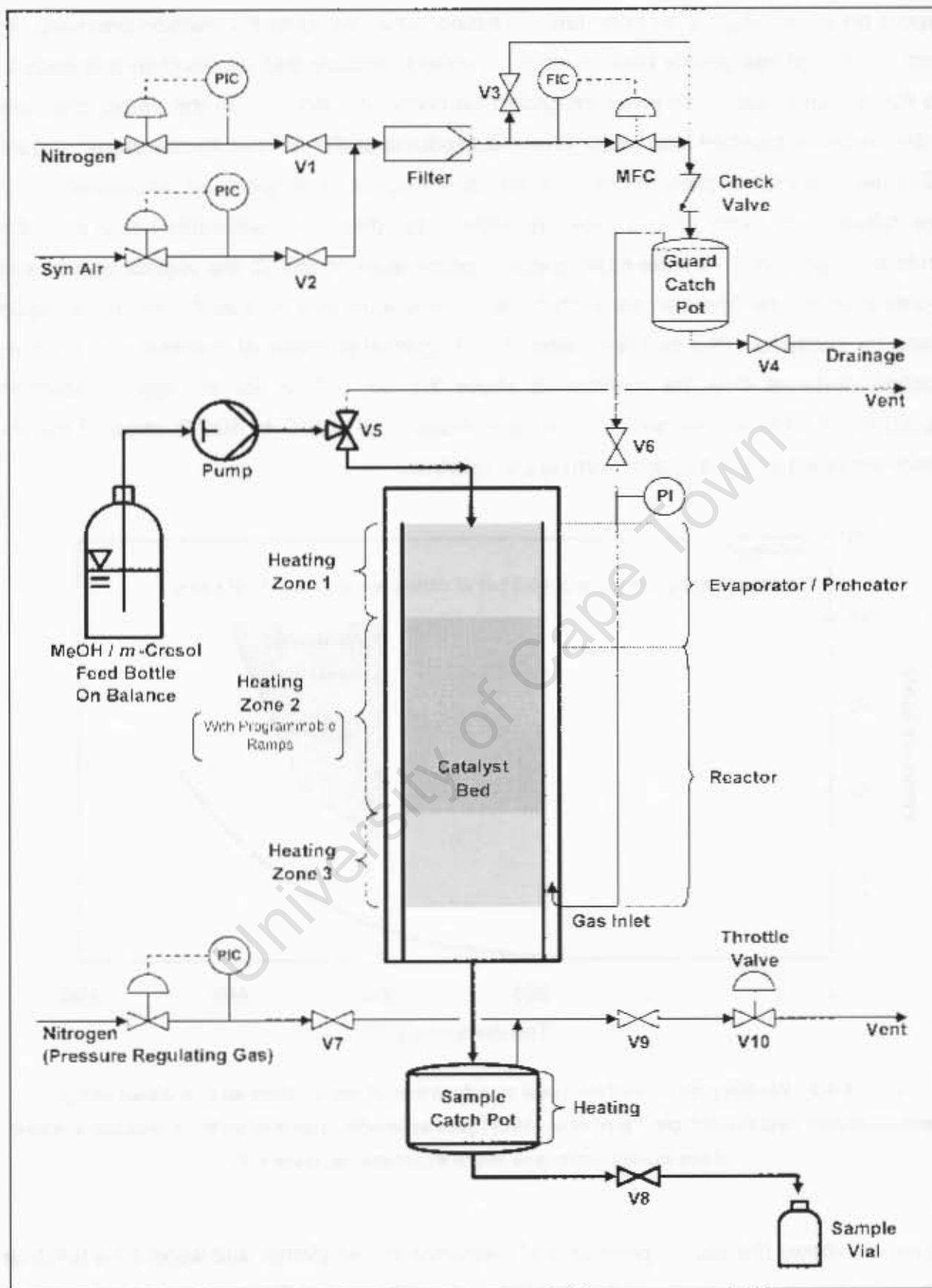


Figure 4-1: Schematic of the experimental apparatus

4.3.3 Vapour pressures of reactants

Vapour pressure (P_{vap}) is an important parameter when deciding on reaction pressure. In case of liquid phase (trickle bed) reaction, in order to ensure that the reaction proceeds in the liquid phase, operating pressure should be controlled higher than the partial pressure of the *m*-cresol reactant and major phenolic products at the desired temperature. Figure 4-2 shows the vapour pressure of *m*-cresol as a function of temperature, calculated using data taken from Perry (1997) (see appendix 1 for data and calculation) and also the window of operation. At base case reaction temperature of 350°C, the vapour pressure of *m*-cresol would be approximately 16.5 bar. To ensure that *m*-cresol remains in liquid phase for methanol : *m*-cresol feed ratio of 1 : 1, (partial pressure of *m*-cresol was 8.3 bar) reaction pressure must be maintained above 8.3 bar. Thus for the applied reaction pressures of 30 to 80 bar and reaction temperatures of 300°C to 400°C, most of the *m*-cresol remained in liquid phase, wetting the catalyst.

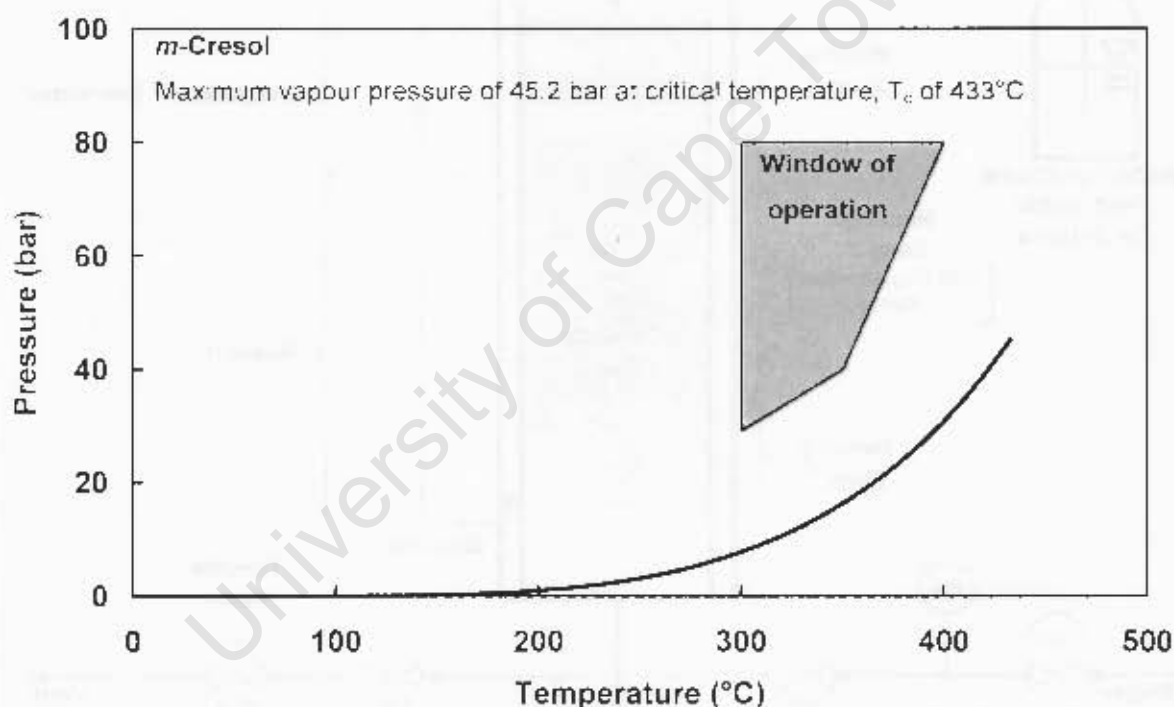


Figure 4-2: Vapour pressure of *m*-cresol as a function of temperature as calculated using thermodynamic data taken from Perry *et al.* (1997) (see appendix 1) as well as the operation window of the experiments (see list of experiments, table 5-4)

Figure 4-3 shows the vapour pressures of methanol, dimethylether and water as a function of temperature, as calculated using data taken from Perry (1997) (see appendix 1 for data and calculations) and also the window of operation. The lowest reaction temperature of 300°C exceeds the critical temperature both methanol and dimethylether, thus these

Methylation of *m*-cresol

compounds were mostly present, supercritically, in the vapour phase although small amounts of each compound would have dissolved into the liquid phase (*m*-cresol). So the reaction, as such, would have occurred in the liquid phase, thus wetting the catalyst.

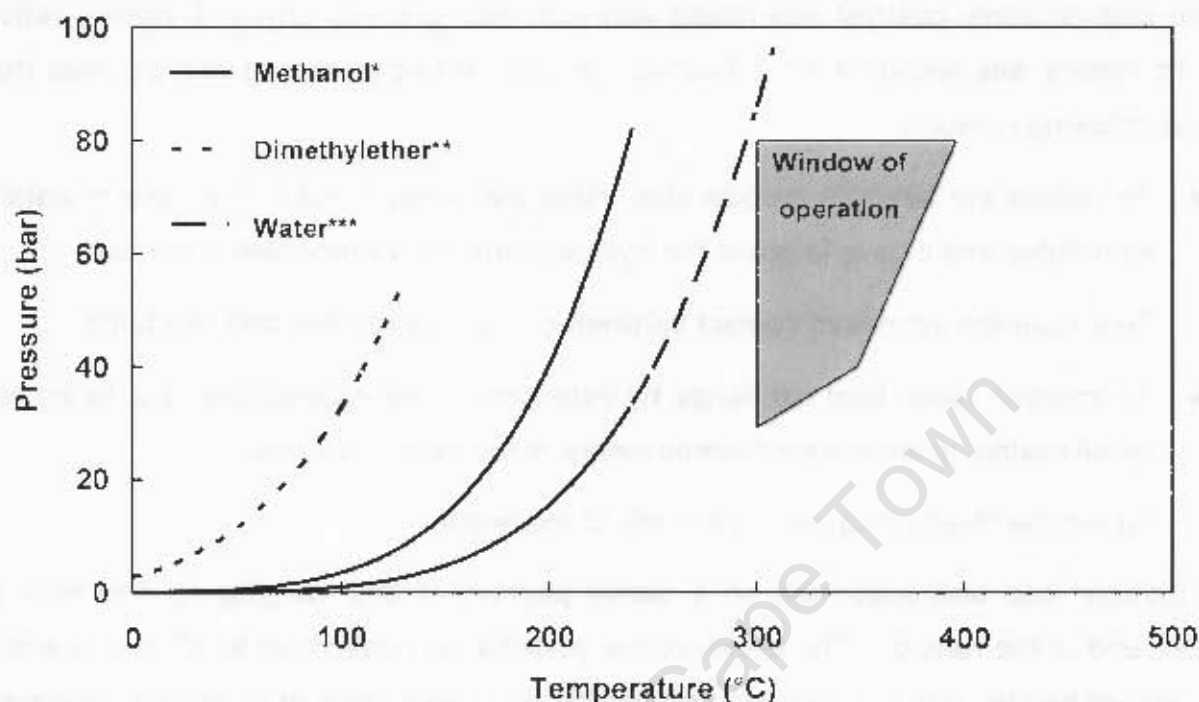


Figure 4-3: Vapour pressure of methanol, dimethylether and water as a function of temperature as calculated using thermodynamic data taken from Perry *et al.* (1997) (see appendix 1) as well as the operation window of the experiments (see list of experiments, table 5-4).

*Methanol: maximum vapour pressure of 81.4 bar at critical temperature, T_c of 240°C

**Dimethylether: maximum vapour pressure of 52.7 bar at critical temperature, T_c of 127°C

***Water: maximum vapour pressure of 219.4 bar at critical temperature, T_c of 374°C.

4.3.4 Reactor packing and catalyst bed

The methanol evaporated in the evaporator / preheater zone, the top section of the reactor (figure 4-5) while the liquid fraction of the feed (*m*-cresol) trickled over approximately 110 mm SiC packing before reaching the catalyst bed. The catalyst bed was located this far down in the reactor for the following reasons:

- To keep the inlet temperature lower than the boiling temperature of the methanol at the reaction pressure (see sections 4.3.2 and 4.3.7.4)
- To evaporate the volatile part of the feed mixture (methanol) within the SiC packing at low temperatures, without overheating, to ensure steady evaporation
- To keep the inlet temperature low to reduce coking in the feed line (also see section 4.3.7.4)

- To encourage uniform feed dispersion at the beginning of the catalyst bed and throughout the entire cross-section of the reactor
- To preheat the feed to reaction temperature

In the catalyst zone, catalyst was mixed with inert SiC ($\phi \leq 930 \mu\text{m}$) in a volume ratio of 1:1 (for details, see section 4.4.1). Diluting the catalyst bed by mixing with SiC was done for the following reasons:

- To reduce the effective particle size within the catalyst bed in the case of catalyst extrudates and thus to improve the hydrodynamic flow properties in the bed
- To encourage increased contact between catalyst extrudates and reactants
- To improve radial heat exchange by extension of the catalyst bed and to improve radial mixing, given the exothermic nature of the main reactions
- To reduce channelling along the walls of the reactor

The catalyst bed was supported on a carrier packing of SiC, ranging 40 mm from the bottom end of the reactor. The length of this packing was optimised to 40 mm to ensure the catalyst bed lay within a zone where reaction could take place in conditions as close to isothermal as possible (see section 4.3.7.4).

4.3.5 Sample catch pot

Liquid product and unconverted liquid reactant continued trickling through the reactor and upon exiting cooled by air cooling before being collected in a 200 ml sample catch pot. The sample catch pot had two outlets:

- A gas outlet to vent on top of the catch pot. Any gases produced in the reaction (e.g. dimethylether from methanol) were expelled through the throttle valve to vent (see figure 4-1). The pressure control gas (see section 4.3.5 for details) joined this line before the throttle valve.

No gaseous product was analysed as conversion and selectivities were calculated on a phenolic ring balance basis.

Positioning the throttle valve after the catch pot and feeding in the pressure control gas after the catch pot was done in order to knock out all the condensable products and avoid flushing this product.

- Any liquid product present in product mixture was collected in the sample catch pot and was regularly transferred into sample vials through valve V8 (see figure 4-1).

When drawing samples, care was taken to ensure no liquid product remained in the sample catch pot and reaction pressure did not drop.

While the pressure in the sample catch pot equalled the reaction pressure, temperature was maintained at 60°C to prevent both possible solidification of heavier products (which have higher melting temperatures) and flashing off lighter products (which could happen at temperatures above 60°C).

4.3.6 Pressure control

Pressure control was achieved through the introduction of a back pressure regulating gas (nitrogen) into the effluent gas stream downstream of the sample catch pot. A valve with a regulating stem (throttle valve, see figure 4-1) was employed to throttle this combined gas stream before venting to exhaust, such that the pressure in the reactor was maintained by the delivery pressure of the pressure regulating gas.

4.3.7 Reactor

4.3.7.1 Reactor body

A schematic representation of the reactor is provided in figure 4-4. The reactor body consisted of a 225 mm long stainless steel tube with an external diameter (O.D.) of 19 mm. The internal diameter (I.D.) was 16 mm. A thermowell, with external diameter of $\frac{1}{8}$ ", rising up from the bottom of the reactor, was located in the centre of the reactor. Inside this thermowell a thermocouple could be moved up and down to measure the temperature profile of the reactor. During experiments, this thermocouple was positioned right in the middle of the catalyst bed. The reactor had an effective volume of 2.3 cm³ per cm length. A gauze at the bottom of the reactor prevented any packing from falling out. The internal reactor tube was fastened by Reactor Fastening Nut to an outer shell with an external diameter of 25 mm (I.D. was 22 mm). There was space of 1.5 mm between the internal reactor tube and the outer shell through which gas from the gas inlet (right side, close to bottom) could travel up and into the packing as for catalyst activation and inertisation of the apparatus.

4.3.7.2 External tube with heating elements

The outer reactor shell sat coaxially in three external tubes (external diameter 38 mm) that carried the heating elements. The heating elements sat flush alongside the reactor outer shell wall.

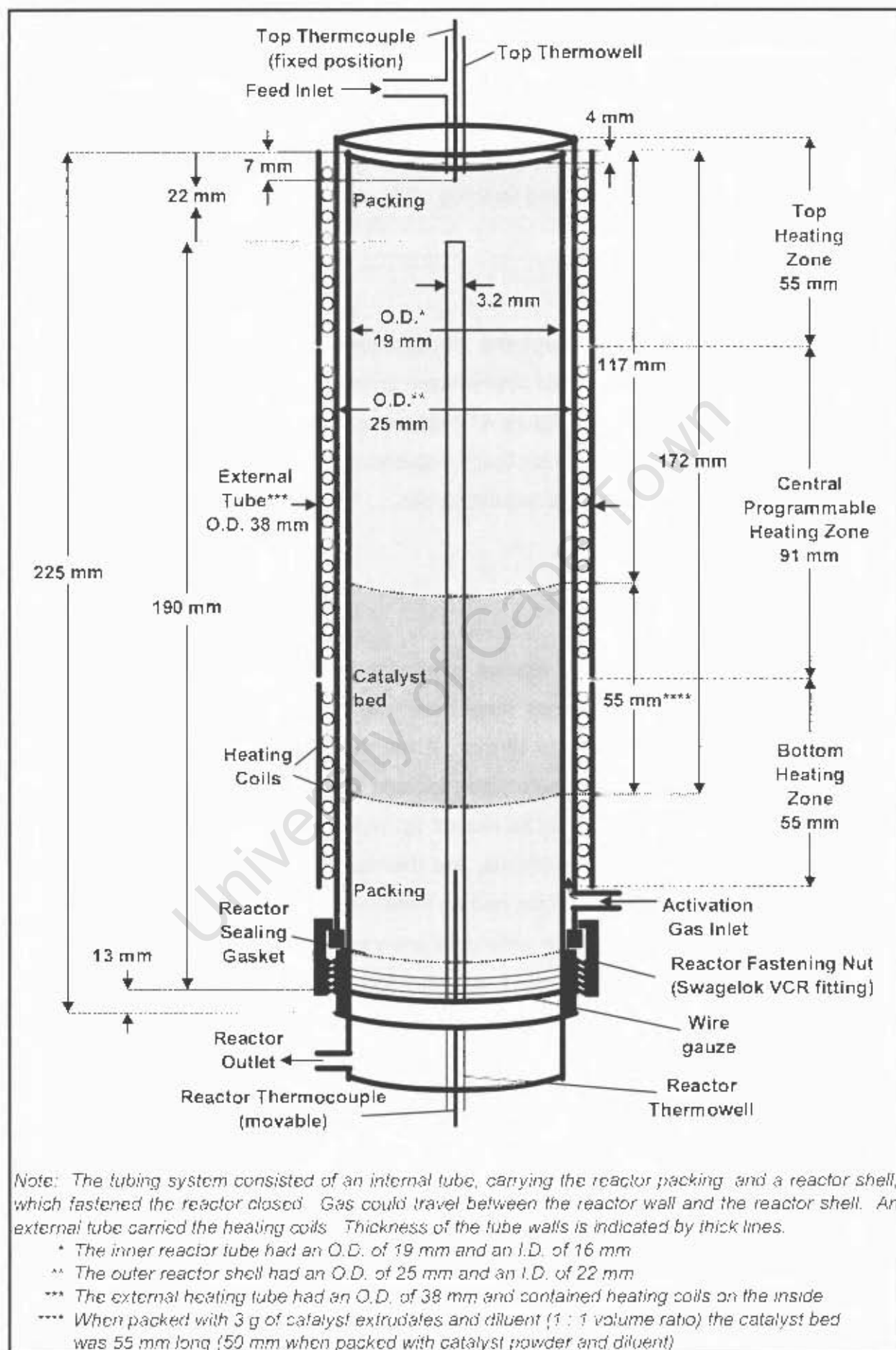


Figure 4-4: Schematic representation of reactor

4.3.7.3 Heating zones

Along the reactor there were 3 heating zones. The first heating element (Zone 1) extended 55 mm, heating the top section of packing. The second heating element (Zone 2) extended a further 91 mm down to the regime in which part of the catalyst bed was situated. The Zone 3 heating element, like Zone 1, extended down a further 55 mm.

Difficulties were experienced with blockages in the feed line at the top of the reactor. This was due to coking in the annular gap between the internal wall of the feed tube and the top thermocouple. In order to reduce coking, the reactor inlet temperature was kept as low as possible. Therefore, the Zone 1 heating element was decommissioned.

The Zone 2 temperature controller was programmable (Gefran 800P Programmable Temperature Loop) and so it was possible to programme gradual temperature increases of the catalyst bed during catalyst activation.

Zone 3 did not have a gradual temperature increase programmable facility. During catalyst drying and activation it was necessary to control the temperature in this zone manually.

4.3.7.4 Reactor temperature profile and “isothermal” catalyst bed

The heating zone settings were manipulated in attempt to obtain temperature profiles that were as isothermal as possible over a length of ca. 60 mm to accommodate the catalyst bed zone (see table 4-3 for exemplary temperature settings).

Figures 4-5a and 4-5b show examples of temperature profiles down the reactor at two different isothermal zone average temperatures, 300°C and 350°C, with corresponding heating coil settings given in table 4-3. For an isothermal zone setting of 350°C the temperature ranged between 344°C at the start of the catalyst bed to a maximum of 357°C near the middle of the bed and then to 345°C at the exit from the bed (figure 4-5b). For an isothermal zone setting of 300°C the temperature ranged between 302°C at the start of the catalyst bed to a maximum of 308°C near the middle of the bed and then to 294°C at the exit from the bed (figure 4-5a).

Due to the need to keep the inlet lines as cool as possible (see sections 4.3.2, 4.3.4 and 4.3.7.3) temperature gradients, in the “isothermal” zone, were larger than desired. However, care was taken, to ensure that the temperature profiles were as equal as possible for the different experiments.

Table 4-3: Temperature Settings of Heating Coils

Isothermal zone average	300°C	350°C
	Temperature Settings	
Heating Zone		
1	Off	Off
2	310°C	359°C
3	315°C	370°C

During experimental runs the temperature profile was checked from time to time and changes were made, if required, to adjust the catalyst bed temperature profile.

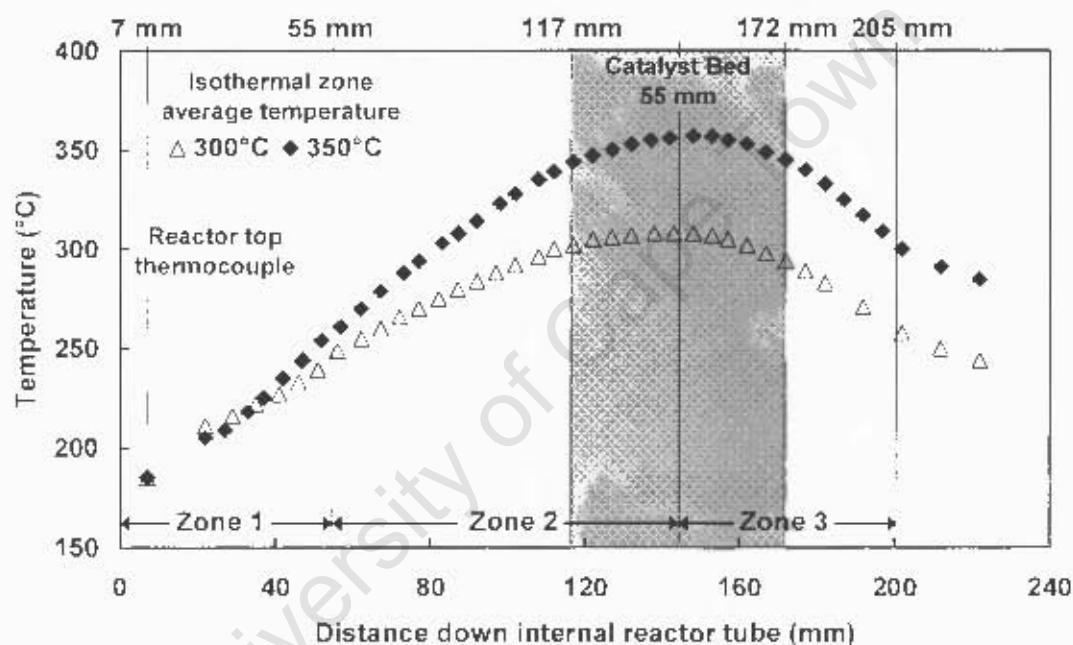


Figure 4-5a: Optimised temperature profiles down the reactor for two different isothermal zone average temperatures. The temperature profiles pertain to catalyst in extrudates form. For powder catalyst, the catalyst bed was slightly shorter (approximately 50 mm in length)

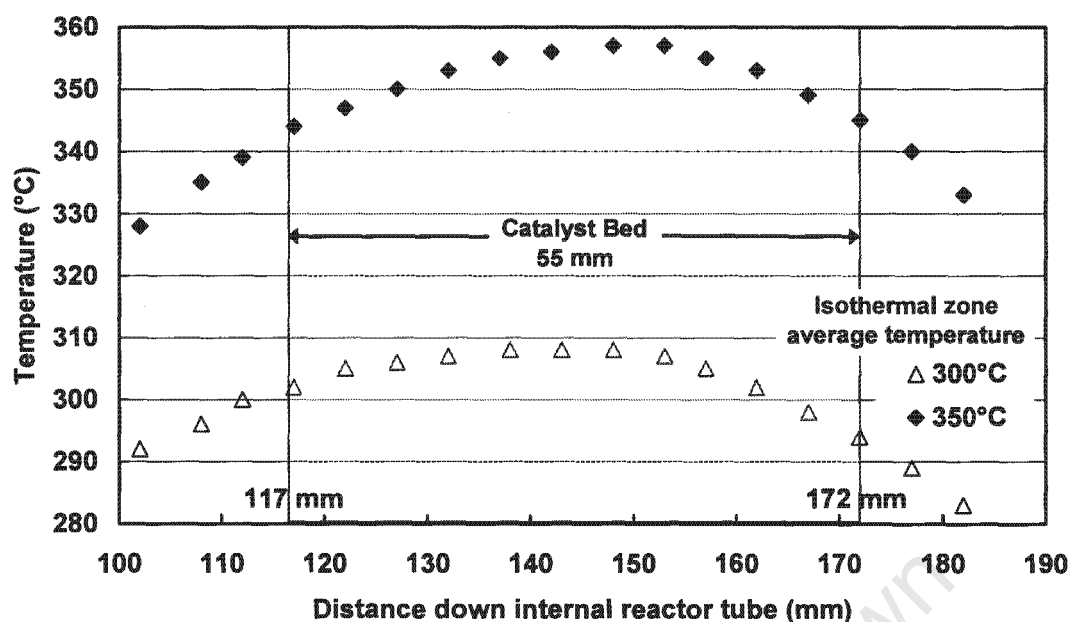


Figure 4-5b: An expanded view of the optimised temperature profiles down the reactor for two different isothermal zone average temperatures, as shown in figure 4-5a. The temperature profiles pertain to catalyst in extrudates form. For powder catalyst, the catalyst bed was slightly shorter (approximately 50 mm in length)

Figure 4-6 shows examples of temperature profiles for two different experiments (CM D3 and CM D4). The heating zones were manipulated to achieve similar temperature profiles. It can be seen that the temperature profile over the catalyst bed was similar in both cases, differing by less than 2°C at any one position.

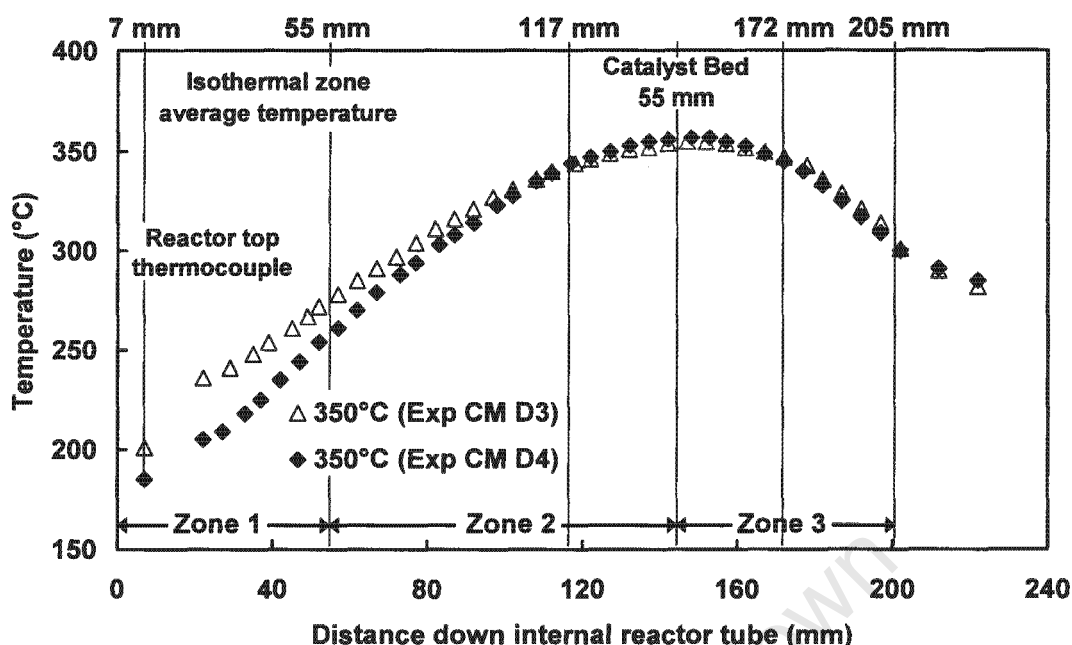


Figure 4-6: Optimised isothermal zone average temperature profile down the reactor for two different experiments, CM D3 and CM D4 for MFI-220 and MFI-90 in extrudates form. For powder catalyst, the catalyst bed was slightly shorter (approximately 50 mm in length)

4.4 Experimental operation

4.4.1 Catalyst loading

The catalyst was packed into the catalyst bed region in a 1:1 volume ratio with SiC. 2.4 g zeolite crystal powder or amorphous silica-alumina was used. Where extrudates were used, it was assumed that catalyst consisted of 20 wt % binder (see table 4-1). Thus 3.0 g of extrudates was used. 3.0 g extrudates in a 1:1 volume ratio mixed with SiC is a slightly larger volume than 2.4 g zeolite powder mixed in the same ratio (12.7 and 11.5 cm³, respectively). To accommodate for this difference all catalyst beds ended 172 mm down the reactor (see figures 4-4 and 4-5). Any additional volume was packed into the top end.

4.4.2 Reactor leak test

Upon assembly, the experimental apparatus was pressurised with nitrogen to operating pressure of 80 bar. Soapy water was applied to all pipe joints, where a leaking joint would encourage bubble growth. Any leaking joints were re-tightened and leak sealed. The pressure within the unit was also monitored over an hour for any pressure drop.

When there was no pressure drop within an hour and no further leaks detected at any of the joints, the experimental apparatus was deemed "pressure tight".

4.4.3 Catalyst drying and activation

Catalyst was dried and activated *in situ*, prior to introduction of feed. Synthetic air, then nitrogen, both at ambient pressure, were passed over the catalyst at a flow rate of $19 \text{ cm}^3 / \text{min}$, i.e. GHSV of between 90 and $100 \text{ ml} / \text{ml} \cdot \text{h}$, respectively, using the mass flow controller (see figure 4-1).

Figure 4-7 illustrates the drying and activation procedure, which was carried out at 1 bar. During the drying phase, catalyst was heated to 90°C , held for 1 hour, heated to 100°C , held for 1 hour, heated to 110°C and held for 1 hour in order to slowly remove moisture. For activation (i.e. removal of other adsorbed compounds) the catalyst was heated to 350°C , where it was held since this was the start up temperature of all experimental series carried out. Each temperature increase was at a rate of 1°C per minute. Once the temperature had reached 350°C , air supply was stopped and nitrogen was introduced, also at $19 \text{ cm}^3 / \text{min}$. Nitrogen flow through the reactor was continued for at least 5 hours.

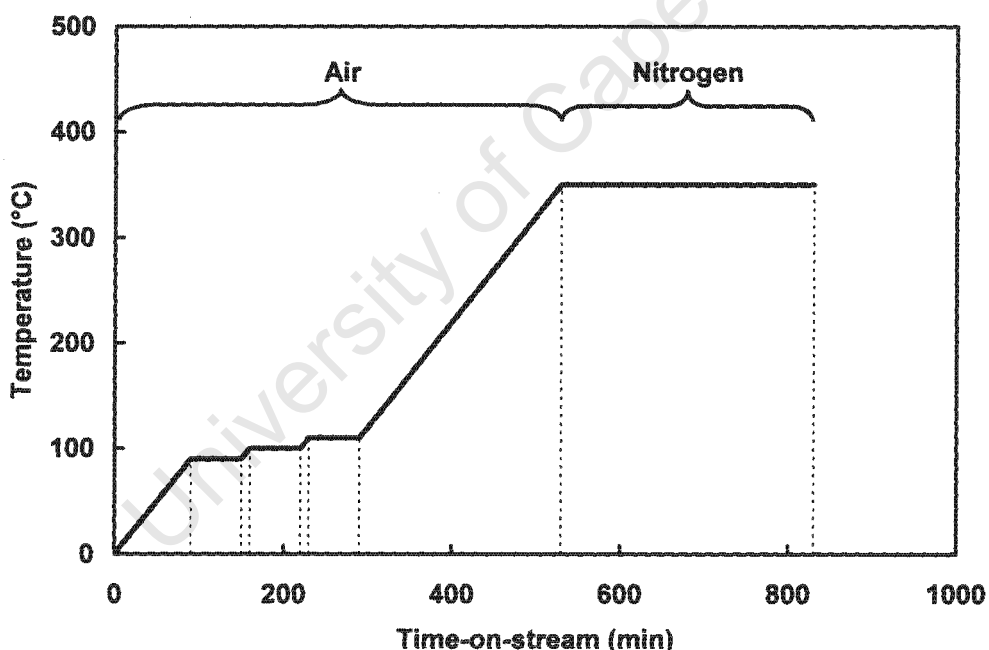


Figure 4-7: Catalyst activation procedure (1 bar, GHSV = $90 - 100 \text{ ml} / \text{ml} \cdot \text{h}$)

4.4.4 Start-up procedure

Following activation of the catalyst, catalyst testing began (refer to figure 4-1).

- Nitrogen flow through reactor was stopped by closing valve V6.
- The experimental apparatus was slowly pressurised from the rear. Valve V7 was opened and pressure control gas was manipulated to supply desired reaction

pressure. The throttle valve was adjusted to limit amount of nitrogen escaping to vent.

- The individual reactor heating zones were adjusted to give desired reactor temperature profile.
- Sample catch pot valve V8 was opened to ensure that any liquid present was drained.
- Feed mixture was purged at the maximum pump rate through the feed pump purge valve (not shown in figure 4-1) until bubble free. Thereafter the feed mixture was bled to the vent via valve V5 also until bubble free.
- The feed valve V5 was switched to the reactor and feed was purged into the reactor with the feed pump still operating at maximum. Maximum feed rate was maintained until the evaporator / preheater thermocouple showed a sharp decline in temperature, indicating that the feed had reached the top of the reactor. Maximum pump rate was maintained for a further 30 seconds, thus allowing the catalyst bed to see feed. The pump rate was then set to a base rate of 0.02 ml / min.
- After approximately an hour, the sample catch pot (via valve V8) was drained again. The reactor temperatures were checked and the temperature profile throughout catalyst bed recorded and adjusted where necessary.

4.4.5 On-line procedures

Experiments were all initiated at base case conditions of 350°C, 80 bar, $WHSV_{m-cresol}$ 0.37 $g_{m-cresol} / g_{active\ catalyst} \cdot h$ and molar feed ratio of 1 (see table 5-1). Catalyst activity was allowed to settle and reach a quasi-steady state (usually within 50 – 100 hours on stream). After each change of condition, the system needed time to stabilise. Normally, steady state results were obtained after about two feed residence times over the catalyst bed. At the base case conditions, residence time was approximately 10 hours (note: liquid phase operation) so that stabilisation time was about 1 day. The major reason for the long stabilisation period was the hold up of liquid in the catalyst bed, the long packed zones of the reactor and the product lines, as well as due to some backmixing in these zones. Towards the completion of experiments, the reaction conditions were reset to base case conditions in order to establish a measure of catalyst deactivation.

4.4.6 Sampling

During experimental runs, samples were drawn batch wise and analysed off-line. Samples were drawn from the sample catch pot, via valve V8 (refer to figure 4-1), and collected in 25 ml glass sample bottles. The bottles were secured closed by way of a metal screw cap with a rubber gasket.

At base case WHSV of $0.3 \text{ g } m\text{-cresol} / \text{g catalyst} \cdot \text{h}$ (pump rate of $0.02 \text{ ml} / \text{min}$) approximately 15 ml of sample was drawn twice a day. For different WHSV, sampling frequency was adjusted so that approximately 15 ml of sample was drawn every time.

Most samples were obtained as an emulsion. The emulsion separated into an organic and an aqueous phase within a few hours when stored at slightly elevated temperature of ca. 50°C .

At each experimental condition at least three subsequent organic phase samples were analysed for similarity before a change in conditions was made. This was to ensure that at least three steady state data points were achieved at each operating condition.

4.4.7 Altering reaction conditions

The reaction conditions were altered during experiments as follows:

- Temperature was varied by altering heating along the reactor. The heating zone settings were manipulated so as to achieve an isothermal zone at set temperature at each setting (see figures 4-5a, b and 4-6)
- Pressure was varied by altering nitrogen control gas pressure on nitrogen pressure cylinder regulator (see figure 4-1)
- Methanol : *m*-cresol ratio was altered by feeding different feed mixtures
- Catalysts were changed by re-packing the reactor
- Weight Hourly Space Velocity (WHSV) was varied by altering the pump setting. During each other parameter setting, WHSV was altered several times in order to obtain different levels of conversion. This was necessary since selectivity of catalysts of different activity and the effect of reaction conditions on selectivity must be compared at similar levels of conversion

4.4.8 Shut-down procedure

The following procedure was adhered to at the end of the experiment (figure 4-1):

- The reactor heating zones were switched off

- The feed pump was switched off and valve V5 closed
- Nitrogen pressure regulating flow was stopped by closing valve V7 and closing the valve on the nitrogen supply cylinder.
- The throttle valve was fully opened and pressure allowed to drop to atmospheric pressure
- Nitrogen flow from the top of the reactor was introduced (valve V6 opened) and reactor was flushed via mass flow controller by-pass valve, V3, and sample catch pot (with valve V8 opened) to remove all volatile matter
- The reactor was allowed to cool down before any further work was done

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4.5 Feed and product analysis

4.5.1 Gas chromatography

4.5.1.1 Sample chromatogram

All product analyses were conducted via Gas Chromatography (for GC conditions, see table 4-4) using an α -Dex 120 capillary column. The α -Dex column is a special "phenolics" column containing a crown ether. The manufacturer recommends the α -Dex column for separating positional isomers, such as cresol and xylenol isomers (see table 4-5 for details).

Table 4-4: GC type and settings

GC type	Varian 3600
Injector head pressure	2.4 bar (abs)
Injector temperature	280°C
Initial column temperature	135°C
Holding time at initial temperature	10 minutes
Temperature ramp rate	10°C / minute
Final temperature	220°C
Holding time at final temperature	15 minutes
Detector	FID
Detector temperature	300°C
Carrier gas	Helium
Volume injected	2 μ l
Split ratio	1 : 100

Only the liquid organic product phase was analysed. Since conversion and selectivities were calculated on a phenols ring balance, the gas phase and aqueous phase, which contained only traces of phenolic compounds, could be ignored.

Table 4-5: GC column properties

Manufacturer	Supelco
Type	Capillary column
Wall material	Fused silica
Length	30 m
Internal diameter	0.25 mm
Phase	α Dex 120*
Film thickness	0.25 μ m
Temperature limits	30°C up to 230°C

*non-bonded, 20 % permethylated α -cyclodextrin, a crown ether, in SPB-35 (35 % diphenyl / 65 % dimethyl siloxane)

Figure 4-8 shows a chromatogram of a product sample. Reference mixtures, containing different amounts of pure components were made up. Portions of the product sample were “spiked” individually with small amounts of these reference mixtures or with pure compounds to exemplify the peaks of different species that may be present in the reaction product. 19 of the peaks in figure 4-9 represent compounds that were identified by spiking (see table 4-6 for identification of these peaks).

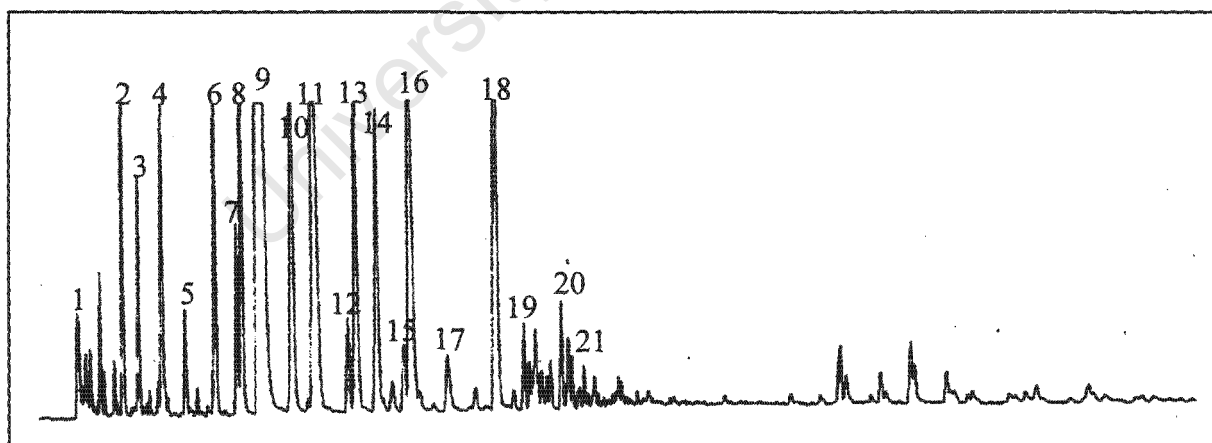


Figure 4-8: Typical sample chromatogram from *m*-cresol methylation with methanol. Small portions of this sample were spiked with pure compounds or mixtures of expected major products for identification purposes (see table 4-6 for corresponding peak identification)

With the GC column used, it was impossible to separate peaks of 3-methylanisole and 4-methylanisole. However, reaction kinetics suggested that 3-methylanisole (by etherification of the feed molecule *m*-cresol) would be by far the more prevalent isomer.

Table 4-6: Identification of peaks within the chromatogram shown in figure 4-8

Peak Number	Species	Identification
1	Methanol	Pure compound
2	Anisole	Pure compound
3	2-Methylanisole	Pure compound
4	3- & 4-Methylanisole*	Pure compounds
5	Phenol	Pure compound
6	o-Cresol	Pure compound
7	2,6-Xylenol	Pure compound
8	p-Cresol	Pure compound
9	m-Cresol	Pure compound
10	2,4-Xylenol	Pure compound
11	2,5-Xylenol	Pure compound
12	2,4,6-Trimethylphenol	Pure compound
13	2,3-Xylenol	Pure compound
14	2,3,6-Trimethylphenol	Pure compound
15	3,5-Xylenol	Pure compound
16	3,4-Xylenol	Pure compound
17	2,4,5-Trimethylphenol	Determined experimentally**
18	2,3,5-Trimethylphenol	Pure compound
19	2,3,4-Trimethylphenol	Determined experimentally**
20	Diphenylether	Pure compound
21	3,4,5-Trimethylphenol	Pure compound

*It was impossible to separate peaks of 3-methylanisole and 4-methylanisole

**It was not possible to obtain 2,3,4-trimethylphenol or 2,4,5-trimethylphenol from commercial sources. However it was possible to deduce the peaks of these components. Analysis of a mixture of the four available trimethylphenol isomers showed two additional fairly prominent but unknown peaks that were ascribed to the missing trimethylphenols. Using reaction kinetics it was possible to identify one of these peaks as 2,3,4-trimethylphenol and the other as 2,4,5-trimethylphenol (see appendix 4-4 for full explanation)

All chromatograms of samples taken during experiments were compared against identified reference chromatograms and by matching peak patterns, peak intervals and / or retention times, the more prominent peaks were identified. However, it was necessary to analyse the reference mixtures fairly frequently because, with time, the GC column properties changed slightly and thus retention times of components analysed also changed slightly.

Unidentifiable peaks were collectively termed "Others". "Others" refers to other alkylated phenol ring products. These would include compounds such as tetramethylphenols, diphenylethers and methylanisoles different from 3-methylanisole.

4.5.2 Response factors and corrected peak areas

The raw sample data reports peak areas (PA_i) as calculated by the GC Flame Ionisation Detector (FID) signal integrator. A peak area represents the integral of the intensity of the FID signal of a peak over time. Thus the peak area is a measure of the amount of carbon eluted with a peak and also of the intensity of carbon atom ionisation within the particular component. The intensity of the FID signal is dependent on the nature of atoms bonded to a carbon atom, as each carbon atom will give a different intensity depending on its environment (e.g. carbon – carbon and carbon – hydrogen give equal signal intensity, while carbon – oxygen gives different, namely lower, signal intensity).

Thus the intensity of the FID signal needs to be corrected for the carbon atoms bound to oxygen atoms in the respective component. The average response factor (f_i) for a particular species considers the different response in the FID of a carbon atom in the molecule that is bound to oxygen atoms. For example, the response of a carbon atom when only bonded to carbon or hydrogen equals 1, but a carbon atom with a single bond to an oxygen atom has been determined experimentally to only have a response of 0.55 and carbon atoms double bonded to oxygen give a response of 0 (Callanan van Steen, 1999). Response factors, f_i , for molecules were calculated on this basis (see section 4.5.2.1). Peak areas of oxygen compounds must be multiplied by these factors to obtain a "corrected peak area", which is proportional to the amount of carbon eluted with that particular peak.

4.5.2.1 Calculating response factors

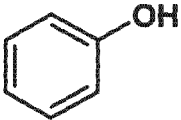
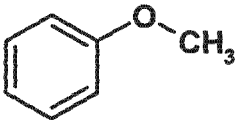
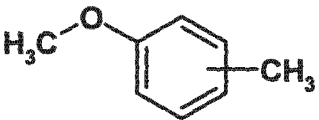
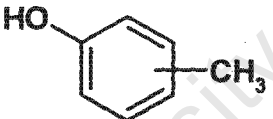
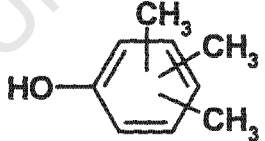
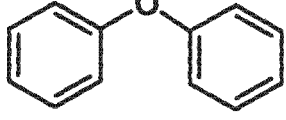
Response factors were calculated by dividing the total number of carbon atoms of the particular compound by the response of these carbon atoms. As an example, the response factor for *m*-cresol ($f_{m-cresol}$) is calculated in equation 4-1.

Equation 4-1: Calculating the response factor ($f_{m\text{-cresol}}$) of *m*-cresol

$$f_{m\text{-cresol}} = \frac{\text{number of carbon atoms in } m\text{-cresol}}{\text{response of carbon atoms of } m\text{-cresol}} = \frac{7}{6 \cdot 1 + 1 \cdot 0.55} = \frac{7}{6.55}$$

Table 4-7 shows the response factors of the feed and major product components.

Table 4-7: Response factors of feed and major products

Species	Molecular Structure	Carbon Atoms			Response Factor (f_i)
		Bonded only to C and H	Single bonded to O	Total Carbon Atoms	
Phenol		5	1	6	$\frac{6}{5 + 0.55}$
Anisole		5	2	7	$\frac{7}{5 + (2 \cdot 0.55)}$
Methylanisole		6	2	8	$\frac{8}{6 + (2 \cdot 0.55)}$
Cresol		6	1	7	$\frac{7}{6 + 0.55}$
Xylenol		7	1	8	$\frac{8}{7 + 0.55}$
Tri-methylphenol		8	1	9	$\frac{9}{8 + 0.55}$
Diphenylether		10	2	12	$\frac{12}{10 + (2 \cdot 0.55)}$

4.5.2.2 Corrected peak areas

The corrected peak (PAC_i) area was calculated through multiplication of the peak area (PA_i) as obtained from GC by the response factor of the particular compound (see section

4.5.2.1 and table 4-7). For *m*-cresol, as an example, the corrected peak area ($PAC_{m\text{-cresol}}$) is calculated from the peak area ($PA_{m\text{-cresol}}$) as shown in equation 4-2.

Equation 4-2: Calculating the corrected peak area ($PAC_{m\text{-cresol}}$) of *m*-cresol

$$PAC_{m\text{-cresol}} = PA_{m\text{-cresol}} \times f_{m\text{-cresol}} = PA_{m\text{-cresol}} \times \frac{7}{6.55}$$

4.5.3 Calculations

In comparing the performance of different catalysts at different operating conditions, conversions, yields and selectivities needed to be calculated. This section details how these calculations were carried out and includes sample calculations.

Table 4-8 shows the data record from a typical sample chromatogram. Calculations were conducted on a phenols ring balance basis where all products, except diphenylether, were treated as mono-cyclic species. Methanol, dimethylether and other light products that are eluted from the GC column before anisole were not considered as cyclic products and therefore not included in the phenols ring balance. Thus, for the accompanying GC report, the first and second detected species (methanol and unknowns 1) are ignored.

Table 4-8 is extended by a column that specifies the composition of the sample (cyclic compounds only) on basis of corrected peak areas and moles (see section 5.3.1).

The calculations in sections 4.5.3.1 to 4.5.3.5 are based on the assumption (and experience) that all phenolic rings that entered the reactor exited it and were detected by the FID.

Table 4-8: Data record from a typical sample chromatogram

Sample			CM-D12-13		
Run			851		
Date			06-Oct-03		
Time			21:43:00		
Peak No.	Peak Name	Retention Time (min)	Area Counts	Area (%)	Content (mol%)
1	Methanol	2.11	19844	1.64	-
2 - 10	Unknowns 1	2.13 - 2.71	22401	1.86	-
11	Anisole	2.84	1348	0.11	0.13
12 - 13	Unknowns 2	3.11 - 3.33	16551	1.37	1.21
14	3-Methylanisole	3.78	47590	3.94	3.99
15 - 16	Unknowns 3	4.44 - 4.65	40501	3.35	2.95
17	Phenol	4.95	1019	0.08	0.11
18	Unknowns 4	5.45	8034	0.67	0.63
19	<i>o</i> -Cresol	5.80	7297	0.60	0.66
20	2,6-Xylenol	6.42	2894	0.24	0.23
21	<i>p</i> -Cresol	6.50	11203	0.93	0.74
22	<i>m</i> -Cresol	6.78	737919	61.12	67.08
23	2,4-Xylenol	7.91	18835	1.56	1.49
24	2,5-Xylenol	8.46	73397	6.08	5.79
25	2,4,6-TMP	9.47	1414	0.12	0.10
26	2,3-Xylenol	9.61	29956	2.48	2.36
27	2,3,6-TMP	10.26	10308	0.85	0.72
28	3,5-Xylenol	10.77	1116	0.09	0.09
29	3,4-Xylenol	10.88	76125	6.31	6.00
30	Unknowns 5	11.62	5754	0.48	0.65
31	2,4,5-TMP	12.44	40798	3.38	2.84
32	2,3,5-TMP	13.18	9879	0.82	0.69
33 - 34	Unknowns 6	13.27	3723	0.31	0.42
35	2,3,4-TMP	13.77	1942	0.16	0.14
36	DPE	14.14	1027	0.09	0.06
37 - 43	Unknowns 7	14.28	16400	1.36	0.92
Total			1207275	100.00	100.00
"Others" = Total unknowns (excluding unknown 1)			113364	7.53	6.78

4.5.3.1 Conversion to molar basis

For a phenols ring balance, corrected peak areas (PAC_i) were converted to mol proportional values (PAM_i). PAM_i is effectively peak area over response of carbon atoms in the molecule. Equation 4-3 illustrates this calculation.

Equation 4-3: Converting the corrected peak area ($PAC_{m-cresol}$) to mol proportional value ($PAM_{m-cresol}$) for *m*-cresol

$$PAM_{m-cresol} = \frac{PAC_{m-cresol}}{\text{number of carbon atoms in } m\text{-cresol}} = \frac{PA_{m-cresol}}{7} \times \frac{7}{6.55} = \frac{PA_{m-cresol}}{6.55}$$

This was converted to molar fraction by dividing through the sum of mol proportional values (see yield, section 4.5.3.2). Corresponding data is given in the last column of table 4-8).

4.5.3.2 Yield

The molar yield of a product (equivalent to its molar fraction) is calculated by dividing its mol proportional value (PAM_i) by the sum of the mol proportional values ($\sum PAM_i$) of all phenolic components present (reactant and products). Equation 4-4 illustrates these calculations.

Equation 4-4: Calculating molar yield of product A

$$Y_{\text{product A}} = \frac{PAM_{\text{product A}}}{\sum_i^n PAM_i}$$

4.5.3.3 Conversion

The conversion of *m*-cresol is calculated using the sum of the mol proportional values (PAM_i) of *m*-cresol and of each of the phenolic products. Equation 4-5 illustrates this calculation.

Equation 4-5: Calculating conversion of *m*-cresol

$$X_{m\text{-cresol}} = 1 - \frac{PAM_{m\text{-cresol}}}{\sum_i^n PAM_i}$$

4.5.3.4 Selectivity

The molar selectivity of a product is calculated by dividing its mol proportional value (PAM_i) by the sum of the mol proportional values of all phenolic products. Equation 4-6 illustrates this calculation.

Equation 4-6: Calculating molar selectivity of product A

$$S_{\text{product A}} = \frac{PAM_{\text{product A}}}{\left(\sum_i^n PAM_i \right) - PAM_{m\text{-cresol}}} = \frac{Y_{\text{product A}}}{X_{m\text{-cresol}}}$$

4.5.3.5 Relative distributions

Data evaluation comprises compound distributions, a kind of relative selectivity, i.e. the content of a certain compound or group of compounds in a certain fraction of the total product, such as xylenols in total phenolics product or xyleneol isomers distribution in the xylenols fraction. Equation 4-7 gives an example, where the relative selectivity of xyleneol A ($C_{\text{xyleneol A}}$) within the total xyleneol product is calculated using the mol proportional values (PAM_i) of all xylenols produced in the reaction.

Equation 4-7: Calculating xylenols distribution, for example
relative selectivity of xyleneol A within xyleneol product

$$C_{\text{xyleneol A}} = \frac{PAM_{\text{xyleneol A}}}{\sum_i^n PAM_{\text{xyleneol i in product}}}$$

4.6 GC error

There are two possible sources of error in GC analyses of samples. It is possible that peaks may be misidentified as GC column properties can change slightly with time. For this reason the reference mixtures were frequently analysed. At times the carrier gas supply pressure (and consequently the column head pressure) declined. In such circumstances, integrated areas of peaks became substantially less. For this and other reasons any strange looking analyses were disregarded and samples were reanalysed.

The natural GC scatter was also investigated. The same sample was injected into the GC four times. It was found that there was very little difference between each reading (table 4-9).

Table 4-9: Determination of GC error of major peaks (sample 13 from CM D11, 4 analyses)

		Average (mol %)	Standard Deviation (mol % points)	Relative Deviation (%)
Conversion		62.0	0.09	0.14
Yield	3-Methylanisole	11.0	0.20	1.82
	2,5-Xyleneol	10.4	0.05	0.48
	3,4-Xyleneol	6.2	0.01	0.16

5. Results

5.1 Preliminary findings

Preliminary experiments were conducted, during which experimental parameters were varied to determine appropriate “base case” conditions. All subsequent experiments were initiated at these conditions and parameters were varied about base case conditions (as shown in table 5-1).

As discussed in previous sections, experiments were conducted at high pressure (30 – 80 bar) to ensure the reaction was carried out with *m*-cresol in liquid phase for operating temperatures of 300°C – 400°C (see figure 4-2).

WHSV was defined as the mass of reactant (*m*-cresol) per mass of “active catalyst” (zeolite or amorphous silica-alumina) per hour and was calculated on *m*-cresol feed basis. At base case conditions, WHSV was $0.37 \text{ g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$.

Table 5-1: Reaction Base Case Parameter Values

Parameter	Base case value	Range
Mass of active catalyst, g	2.4*	2.4 – 9.6**
Temperature, °C	350	300 – 400
Pressure, bar	80	30 – 80
Methanol : <i>m</i> -cresol feed ratio (molar)	1 : 1	0.5 – 2.0
WHSV, $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}^{**}$	0.37	0.07 – 2.8
Pump rate, ml / min	0.02	0.01 – 0.32

*In case of extrudates, 3.0 g of catalyst applied assuming 20 mass % binder

**One experimental campaign was conducted over 9.6 g of active MFI-90, fourfold the usual mass. This was done in order to conduct the reaction at low WHSV of $0.07 \text{ g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$, which could not be achieved anymore by setting the pump rate to the respective low level (limited to minimum of 0.01 ml / min)

In experiments testing performance of catalysts in extrudate form, it was assumed that 20 wt % of the extrudates consisted of binder (Fletcher, 2002). Thus, in order to compare the performance of extrudates with that of pure crystal powder catalyst, 3.0 g of extrudates were loaded into the reactor. Weight Hourly Space Velocity is therefore always defined as $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$.

5.1.1 Blank experiment

A blank run was performed in order to determine the amount of reaction that occurs in the absence of active catalyst, i.e. when feed comes into contact with the experimental apparatus, such as the reactor wall or the SiC diluent. The blank experiment was carried out at base case conditions (350°C, 80 bar, MeOH : *m*-cresol molar feed ratio of 1 and pump rate of 0.02 ml / min) over SiC packing.

Table 5-2 compares the yield distribution of blank run products to impurities present in the feed. An equivalent conversion of 0.7 % was achieved in the blank run. Blank conversion was disregarded in overall conversion calculations.

Table 5-2: Results from Blank Run

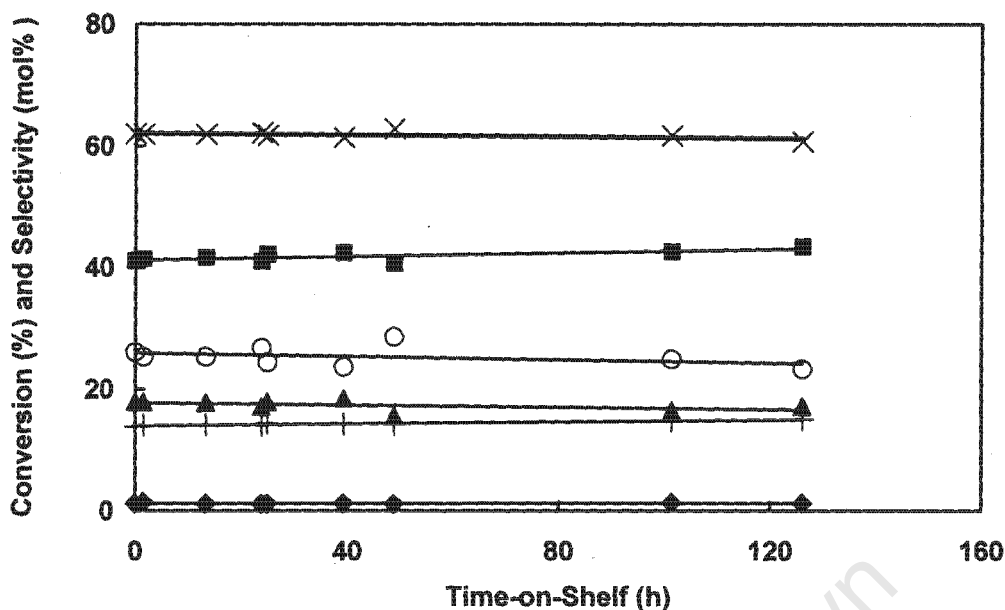
Component	Abundance (mol %)	
	Feed	Blank run
<i>m</i> -Cresol	99.3	98.6
<i>p</i> -Cresol	0.6	0.6
Xylenols	-	0.4
3-Methylanisole	-	0.3
Others*	0.1	0.1
Total	100.0	100.0

*Evaluated like cresols

5.1.2 Sample stability

As samples were not analysed online, samples could not always be analysed immediately. There were occasions when samples stood for 2 to 3 days in 25 ml bottles under air, closed with a metal lid and rubber sealing, before it was possible to conduct analyses. The stability of the samples over time was investigated to determine whether such time delays between sample taking and sample analysis would affect the result.

Figure 5-1 shows a set of sample analyses that were carried out over 126 hours. Analyses did not show any appreciable trends in sample composition change, thus indicating that sample deterioration over time was not a problem. Table 5-3 shows the slopes of the trend lines in figure 5-1. It can be seen that the gradients of these lines are so small that disparity is most likely due to experimental scatter.



× Conversion ■ Xylenols + TMPs ◆ o- & p- Cresol ▲ 3-Methylanisole ○ Others

Figure 5-1: Sample stability over 126 hours for *m*-cresol conversion and product selectivities versus time product sample spent sitting on shelf

Table 5-3: Sample stability over 126 hours

Parameter	Slope of trend line
Conversion	-0.01
Xylenols	0.02
TMPs	-0.01
o- & p-Cresols	-0.01
3-Methylanisole	0.01
Others	0.00

5.1.3 Catalyst stability

5.1.3.1 Initial deactivation

In the course of experimental campaigns, catalyst stability was investigated. It was found that all catalysts tended to loose some activity, although the magnitude of activity loss was dependent on reaction conditions and differed from catalyst to catalyst.

At the beginning of runs, it was observed that conversion declined appreciably over the initial 50 to 70 hours before reaching a quasi-steady state. For instance, over BEA-150 conversion decreased from 77 % to 71 % during the first 70 hours on stream and over

FER-20 conversion decreased from 45 % to 28 % over the same period (figures 5-2 and 5-3).

The first data point in each of figures 5-2 and 5-3, where conversion was lower, reflects unconverted amounts of feed that was still present in downstream sections of the experimental apparatus at experiment start-up.

Samples analysed over this dynamic period were not used in catalyst or condition effect comparison. Only samples obtained at steady state periods were compared. All data points in subsequent figures were collected from samples drawn during periods of pseudo steady state catalyst activity. For each different experimental setting, at least three data points were collected after the product composition had stabilised following a change in reaction conditions. Thus each point in experimental evaluation represents the average value of at least three data points obtained under stable operation.

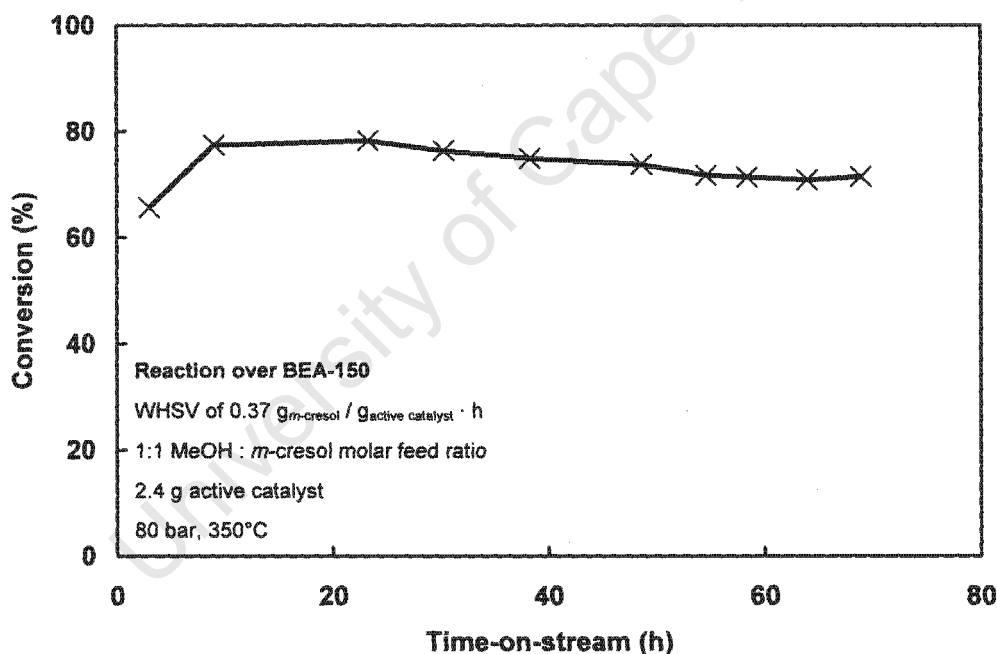


Figure 5-2: Catalyst deactivation during the first 50 – 100 hours of reaction for a rapidly stabilising catalyst (BEA-150)

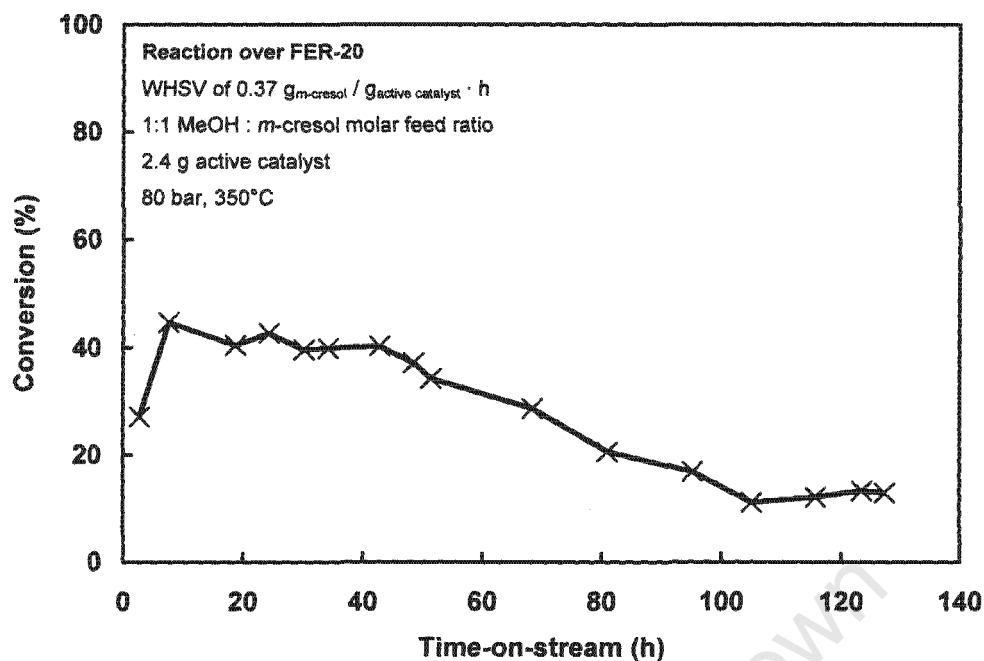


Figure 5-3: Catalyst deactivation during the first 50 – 100 hours of reaction for an initially rapidly deactivating catalyst (FER-20)

5.1.3.2 Increase of catalyst stability at lower temperatures

Of the parameters investigated, temperature had the greatest effect on stability. Decrease in activity was most rapid when reactions were run at higher temperatures.

Figure 5-4 shows the effect on conversion when reaction temperature was increased from 350°C to 400°C, without changing other variables, for methylation over FER-20. Conversion decreased and stabilised at a level lower than that which it had been with reaction temperature of 350°C.

A different trend was observed over MFI-90 (see figure 5-5). At reaction temperature of 350°C conversion continued to decline slightly. Although absolute conversion fell when the reaction temperature was decreased to 300°C, the reaction showed more stability.

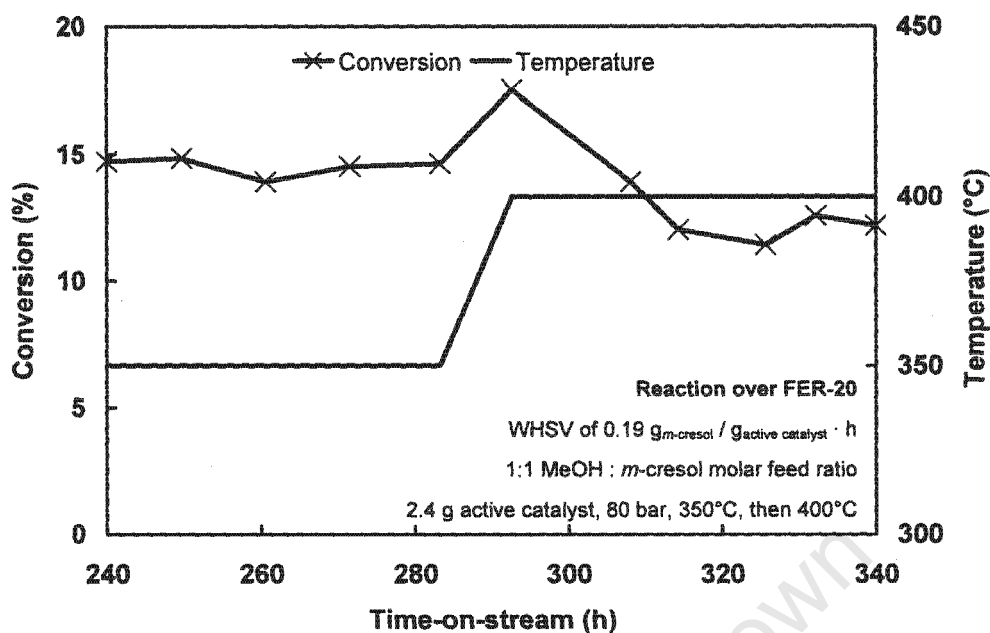


Figure 5-4: Catalyst deactivation at different temperatures for reaction over FER-20. Conversion fell as reaction temperature increased from 350°C to 400°C.

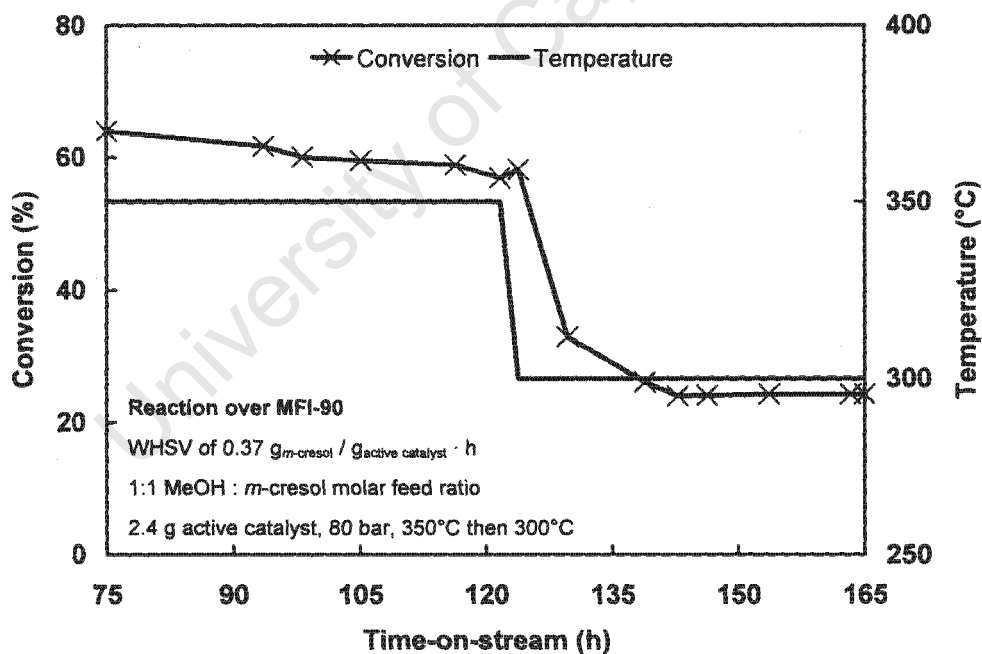


Figure 5-5: Catalyst deactivation at different temperatures for reaction over MFI-90. Conversion stabilised on a lower level as reaction temperature was decreased from 350°C to 300°C.

5.1.4 Experimental reproducibility

Experimental reproducibility is important in establishing the integrity of experimental procedures and apparatus. To test for reproducibility, reactions were repeated at identical reaction conditions over both MFI-220 extrudates and BEA-150 zeolite powder. In each

reproduced experiment, for both MFI-220 and BEA-150, the catalyst was removed from the reactor and an identical quantity of fresh catalyst was re-packed for the reproduced experiment. Figure 5-6 shows selectivity to xylenols versus conversion for the reproduced experiments (also refer to section 6.1.6).

In both reproduced experiments, the results show that similar selectivities were achieved at comparable levels of conversion for each reproduced run. Reproducibility indicates that results obtained in different experiments can be compared at a reasonable level of precision.

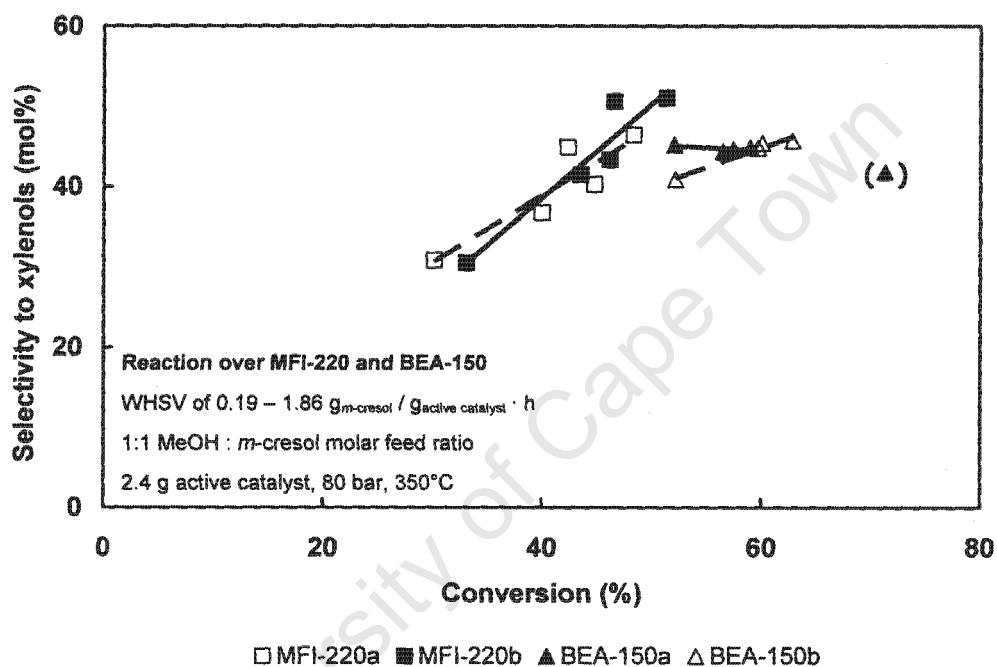


Figure 5-6: Reproducibility over MFI-220 and BEA-150. Figure shows selectivity to xylenols versus conversion at steady state operation.

5.2 Comparison of xylene distribution with thermodynamic data

Product distributions of xylenols over MFI-90 at 300°C and 350°C were compared with thermodynamic equilibrium data obtained at similar conditions by others. Pigman *et al.* (1954) obtained thermodynamic equilibrium composition of the xylene fraction in gas phase at 350°C experimentally over synthetic silica-alumina (see section 2.6.1.1). The thermodynamic equilibrium was also calculated at 350°C for ideal gas phase, using thermodynamic data from Daubert *et al.* (1999), see appendix 1.

The respective experiments were carried out over 2.4 g active catalyst (MFI-90) in trickle phase at operating pressure of 80 bar, methanol : *m*-cresol molar feed ratio of 1 : 1 and WHSV of 0.37 g_{*m*-cresol} / g_{active catalyst} · h. At 300°C, conversion of 32 % was achieved, while at 350°C conversion was 62 %. Xylene distribution results are shown in figure 5-7 in comparison to aforementioned data from literature.

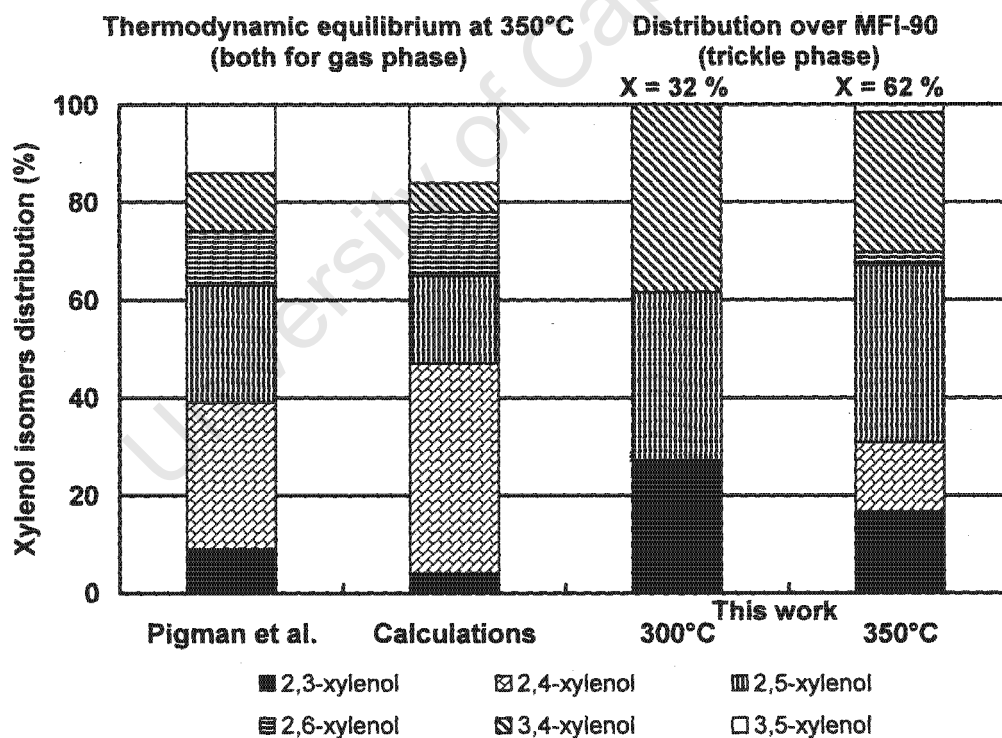


Figure 5-7: Gas phase thermodynamic equilibrium xylene distributions compared with trickle phase xylene distributions from alkylation of *m*-cresol with methanol over MFI-90 (2.4 g active catalyst, 80 bar, methanol : *m*-cresol molar feed ratio of 1 : 1 and WHSV of 0.3 g_{*m*-cresol} / g_{active catalyst} · h) at 32 % and 62 % *m*-cresol conversion respectively

Equilibrium distributions in gas phase are not expected to differ from equilibrium distributions in liquid (or trickle) phase as can be derived from measurements by Imbert *et al.* (1997) and Fritsch *et al.* (2003) who found identical values for the equilibrium distributions of cresols in gas and liquid phase at 380°C.

It can be seen that, at 300°C and medium conversion of 32 %, virtually none of the isomers 2,4- , 2,6- and 3,5-xylenol were produced. At 350°C and high conversion of 62 %, still more 2,5-xylenol (36 %) than 2,4-xylenol (14 %) was formed and higher percentages of 2,3-xylenol (17 %), 3,4-xylenol (29 %) were attained. Percentages of 2,6-xylenol (3 %) and 3,5-xylenol (1 %) remained very low. It is obvious that both distributions were still essentially under kinetic control.

5.3 Catalyst comparison

Catalyst performances were compared at base case conditions to establish which catalyst, if any, exhibited higher selectivity to shape selective products. However, because the activities of catalysts were very different, conversions varied widely (from 9 % to 71 %). Thus it was impossible to compare xylenol selectivities at similar conversions. However, WHSV was varied widely, to get overlapping regions or at least trends that could be extrapolated.

The following graphs (figures 5-8 to 5-47) contain the results as a function of conversion for each of the different products and product fractions that were analysed. Further testing of effect of reaction parameters was conducted over the preferred catalyst, in this case MFI-90 (see sections 5.5.1 to 5.5.4).

5.3.1 Catalyst activity and conversion

Table 5-4 contains a summary of the experimental results. At base conditions, highest activity was observed over zeolites MTW-100 and BEA-150. Amorphous Siral-40 also showed relatively high activity. In contrast, FER-20 and MOR-90 showed low levels of activity. See appendix 3 for data in full.

Table 5-4: Range of and operating parameters employed in different *m*-cresol methylation experiments and range of conversions obtained (refer to appendix 3 for complete data)

Experiment Number	Catalyst	WHSV range (g _{<i>m</i>-cresol} / g _{active catalyst})	Temperature range (°C)	Pressure range (bar)	Molar feed ratio	Conversion at base case (%)	Conversion range (%)*
CM D2	MFI-220	0.2 - 1.9	350	40	1.0	42	30 - 48
CM D3	MFI-220	0.2 - 1.9	350	40	1.0	47	33 - 51
CM D4	MFI-90	0.3 - 3.7	350	40 - 80	0.5 - 2.0	62	25 - 62
CM D5	Blank run**	***	350	80	1.0	0.7	0.7
CM D6	BEA-150	0.2 - 1.9	350	80	1.0	71	52 - 71
CM D7	FER-20	0.2 - 0.4	350 - 400	80	1.0	13	9 - 15
CM D8	MOR-90	0.2 - 0.4	350	80	1.0	23	20 - 28
CM D9	MTW-100	0.2 - 0.9	350	80	1.0	63	48 - 70
CM D10	BEA-150	0.4 - 1.5	350	80	1.0	63	52 - 62
CM D11	Siral-40	0.2 - 1.5	350	80	1.0	56	42 - 63
CM D12	MFI-90	0.2 - 3.5	300 - 350	80	0.5 - 2.0	58	4 - 58
CM D13	MFI-90	0.05 - 1.50****	300	30 - 80	1.0	52	15 - 61

* This does not include initial conversions, i.e. before steady state was reached

** Reaction performed over SiC packing

*** Pump rate of 0.02 ml / min (as per throughput at base case conditions) was maintained

**** For this run 9.6 g of active zeolite instead of 2.4 g, was packed into the reactor

5.3.2 Total xylenols

5.3.2.1 Selectivity to total xylenols

Selectivity to total xylenols varied for the different catalysts tested (figure 5-8). Although, no obvious trend is apparent; most catalysts, as well as the average trend in the figure, show increasing selectivity to xylenols with increasing conversion (slopes of trend lines are also given in figure 5-8). MFI-90 and MFI-220 zeolites showed somewhat higher selectivity to total xylenols than the other catalysts for the range of conversion under investigation.

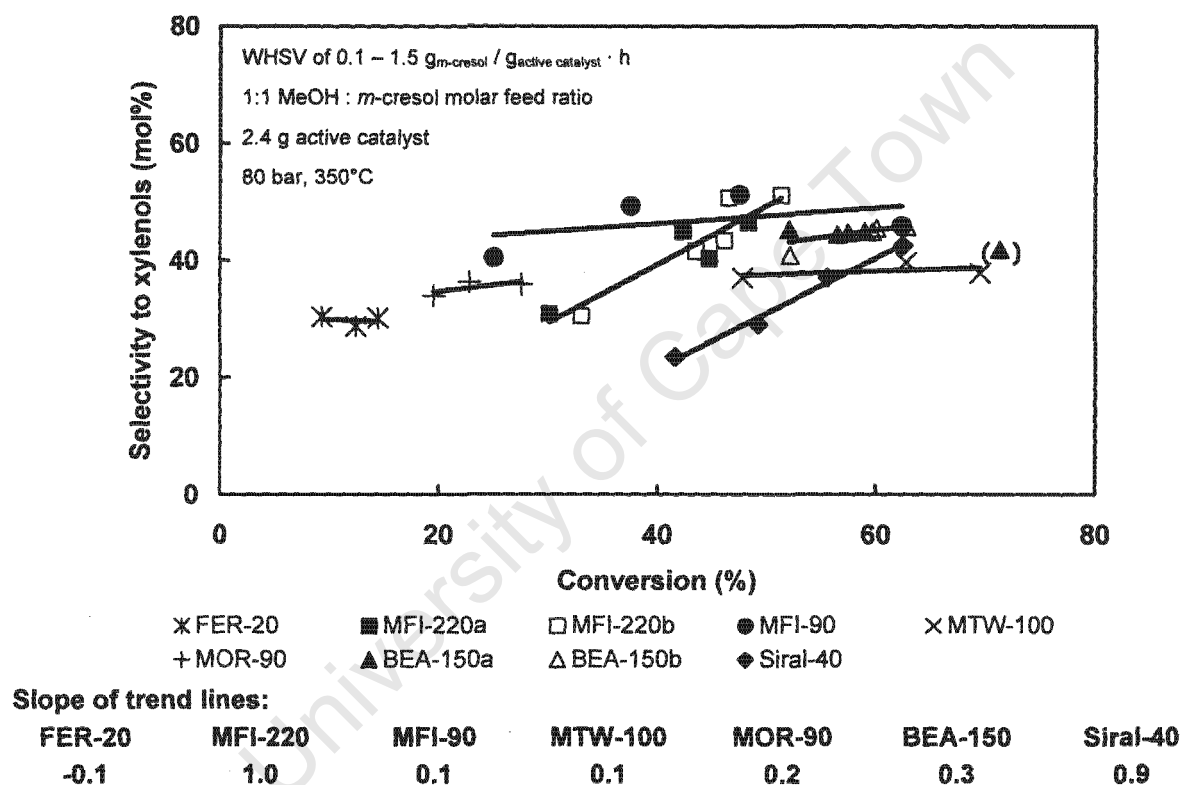


Figure 5-8: Selectivity to total xylenols versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.2.2 Yield of total xylenols

The xylenol yields versus conversions are shown in figure 5-9. It can be seen that all the catalysts exhibit very similar yield to conversion ratios, with trend line slopes (also shown in figure 5-9) of between 0.3 (for FER-20) and 0.8 (for Siral-40 and MFI-220). The other catalysts show trend line slopes of between 0.4 and 0.5.

It can be seen that the xylenol yields increase as conversion increases with a trend line averaging all data points closely matching the origin. The average trend line, shown by

the hatched line in figure 5-9, has a slope of 0.5 reflecting the average selectivity of catalysts towards total xylenols (see figure 5-9). The higher slopes obtained over Siral-40 and MFI-220 indicate that xylene selectivity increases with increasing conversion quicker than over the other catalysts.

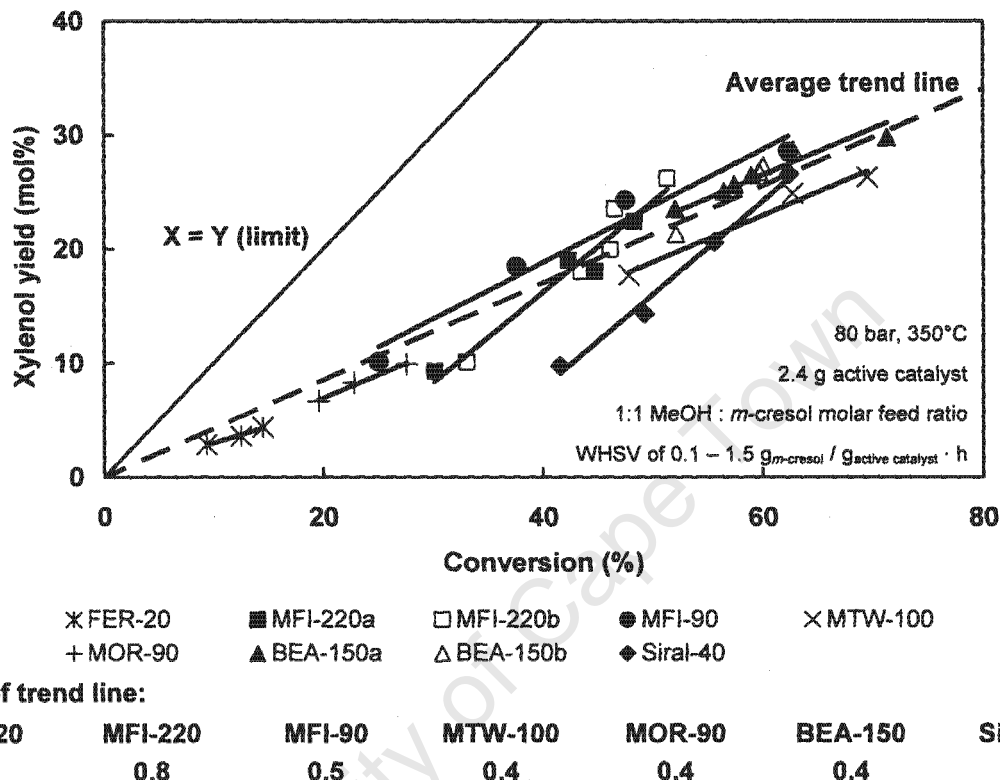


Figure 5-9: Total xylene yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested. The dashed trend line has been forced through the origin.

5.3.3 3-Methylanisole

5.3.3.1 3-Methylanisole selectivity

Selectivity to 3-methylanisole versus conversion is shown in figure 5-10. All catalysts showed similar trends with increasing conversion, namely a steep decline in selectivity to 3-methylanisole. At comparative levels of conversion Siral-40 produced 3-methylanisole at the highest selectivity, although selectivity dropped steeply with increasing conversion. At conversion of 42 % over Siral-40, selectivity to 3-methylanisole was 67 % and when conversion increased to 62 % selectivity to 3-methylanisole fell to 15 % (a gradient of -2.5). Selectivity to 3-methylanisole also dropped very steeply over MFI-220. The other zeolites showed similar trends, but the fall in selectivity to 3-methylanisole was more gradual.

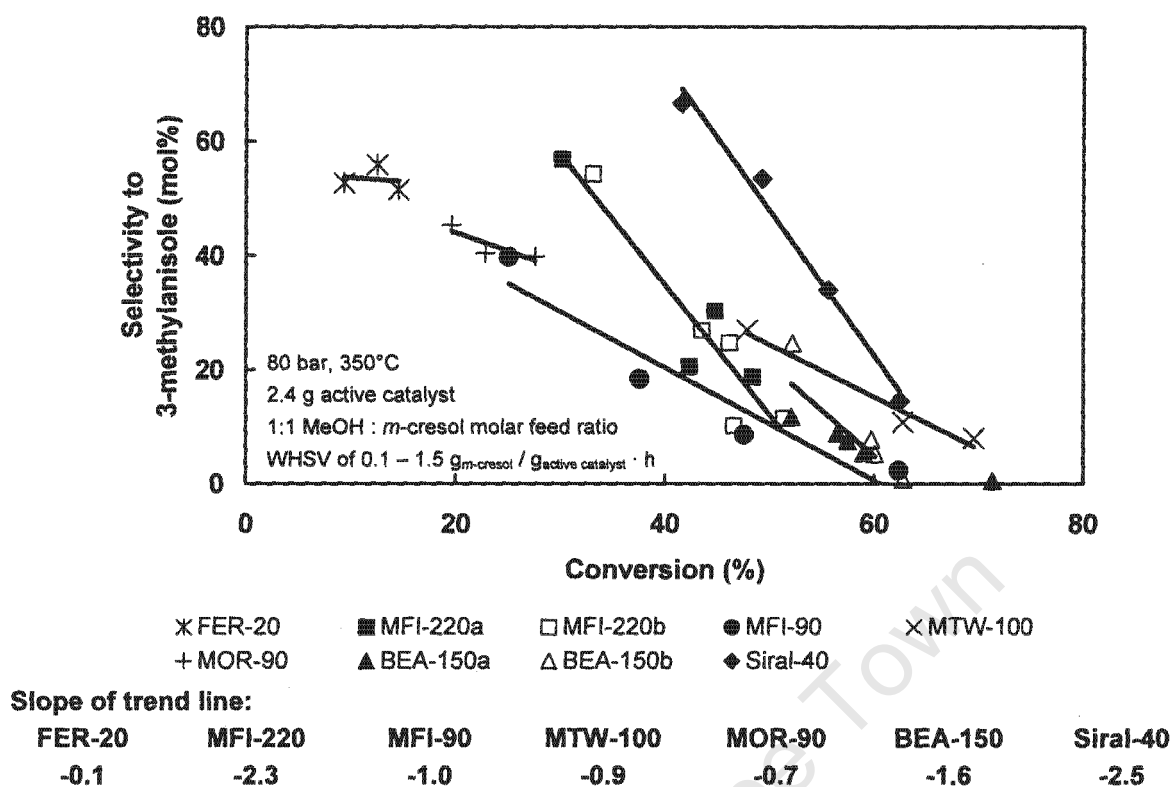


Figure 5-10: Selectivity to 3-methylanisole versus *m*-cresol conversion for *m*-cresol methylation catalysts tested

3-Methylanisole is produced when methylation takes place on the oxygen atom of the *m*-cresol molecule ('O' substitution). As previously discussed (section 2.8.5), it is also possible to easily form two of the xlenol isomers (2,3- and 2,5-xlenol) via internal rearrangement of 3-methylanisole.

5.3.3.2 Yield of 3-methylanisole

Yield of 3-methylanisole versus conversion is shown in figure 5-11.

Siral-40 produced highest yields of 3-methylanisole, although yield dropped sharply as conversion increased (figure 5-11). With 42 % conversion over Siral-40, 28 % of product yield was 3-methylanisole, but at conversion of 62 %, yield of 3-methylanisole dropped to 9 %. MTW-100 and MFI-220 yielded the next highest amounts of 3-methylanisole and although yield also fell with conversion it did not fall as quickly as over Siral-40. MFI-90 produced the lowest yield of 3-methylanisole comparatively. Less active FER-20 and MOR-90 showed still increasing yield of 3-methylanisole with increasing conversion. In contrast the other catalysts tested showed decreasing yields of 3-methylanisole with conversion (but at high levels of conversion) with Siral-40 and BEA-150 showing the

steepest declines. The data indicates that most 3-methylanisole has disappeared at conversion of above 70 %.

The hatched line marks the difference between the limiting line, $X = Y$, and the average trend of xylenols yield in figure 5-9. This line marks, more or less, the edge of 3-methylanisole yield at low conversions.

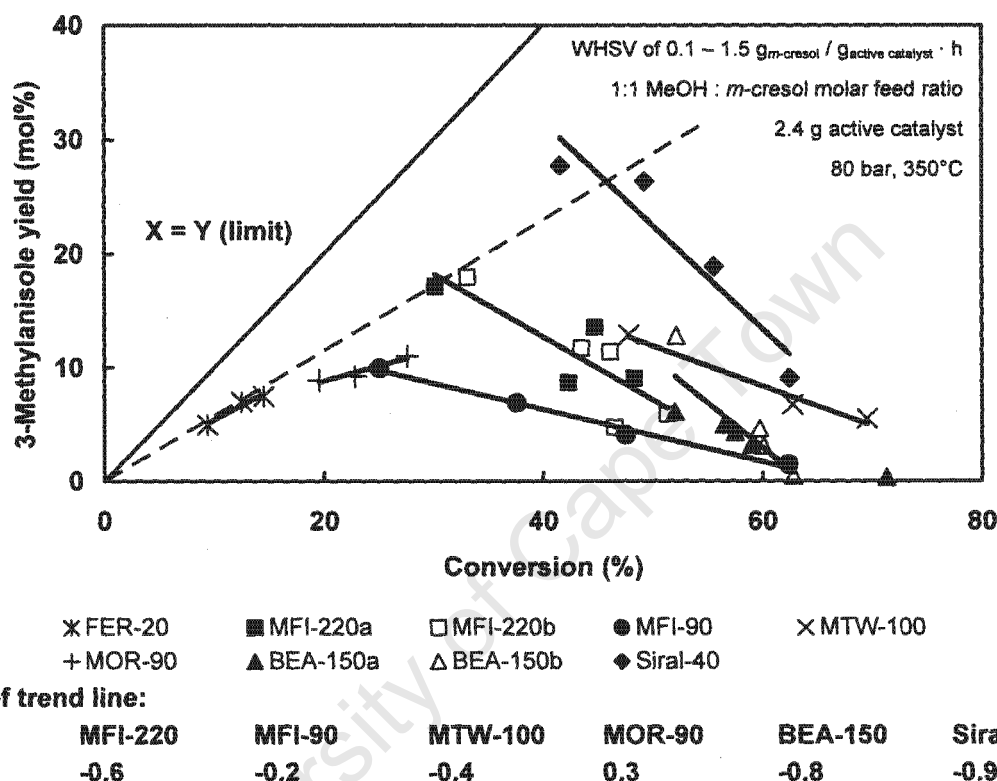


Figure 5-11: 3-Methylanisole yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested. The dashed line has been drawn using the difference between the $X = Y$ line and dotted line in figure 5-9.

5.3.4 Xylenol content in phenolic product

Since 3-methylanisole is a major but, as an ether, a “non-phenolic” by-product, the total reaction product less 3-methylanisole (the “phenolic” product) was plotted against conversion (see figure 5-12) so that this plot represents the content of xylenols within the “phenolic product”.

“Phenolic product” is defined as the proportion of the total reaction product with a hydroxyl group attached to the central ring (i.e. where *m*-cresol has undergone only ‘C’ alkylation and not ‘O’ alkylation). This definition excludes any anisole or methylanisole product, in which the hydroxyl group has already been methylated.

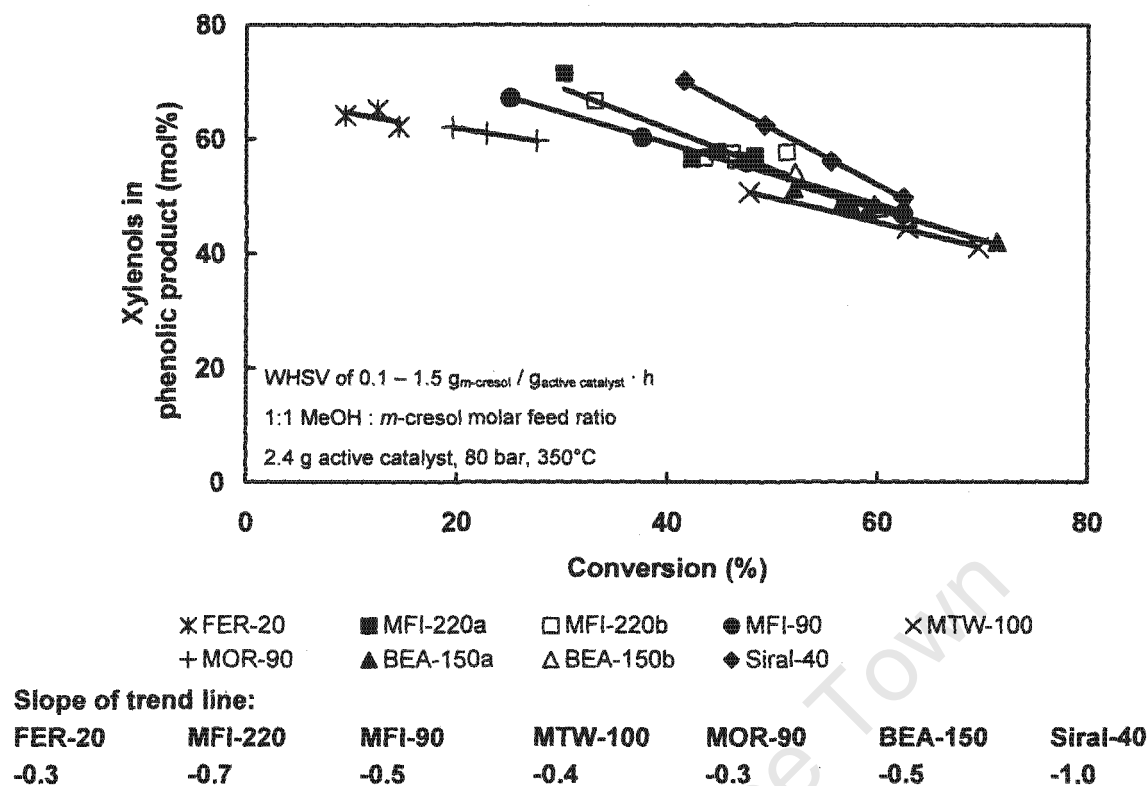


Figure 5-12: Distribution of total xylenols within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

It can also be seen, as a general trend, that catalysts formed decreasing amounts of xylenols within phenolic product with increasing conversion. For MFI-220, for instance, at conversion of 30 %, 71 % of phenolic product comprised xylenols, while at conversion of 48 % only 57 % of phenolic product was xylenols.

It can be seen that Siral-40 produces the highest amount of xylenols within phenolic product. MFI-90, MFI-220, BEA-150 and MTW-100 produced similar levels of xylenols within phenolic product, while FER-20 and MOR-90 showed somewhat lower levels. However, all data points are within a rather narrow band.

5.3.5 Individual xylene isomers

5.3.5.1 2,5-Xylenol

2,5-Xylenol, being more linear than the other xylene isomers, should be more preferred than the other xylene isomers over shape selective zeolites. Hence, it should be possible to evaluate the shape selective effectiveness of the catalysts on *m*-cresol methylation by comparing the proportions of 2,5-xylene produced.

5.3.5.1.1 2,5-Xylenol selectivity

While selectivity to 2,5-xylenol (figure 5-13) varied among catalysts, no obvious trend can be seen. MFI-220 showed the highest selectivity to 2,5-xylenol while Siral-40 showed the lowest. MFI-220 and Siral-40 also showed the highest increase in selectivity with conversion. FER-20 and BEA-150 showed slight decreasing selectivity to 2,5-xylenol with increasing conversion.

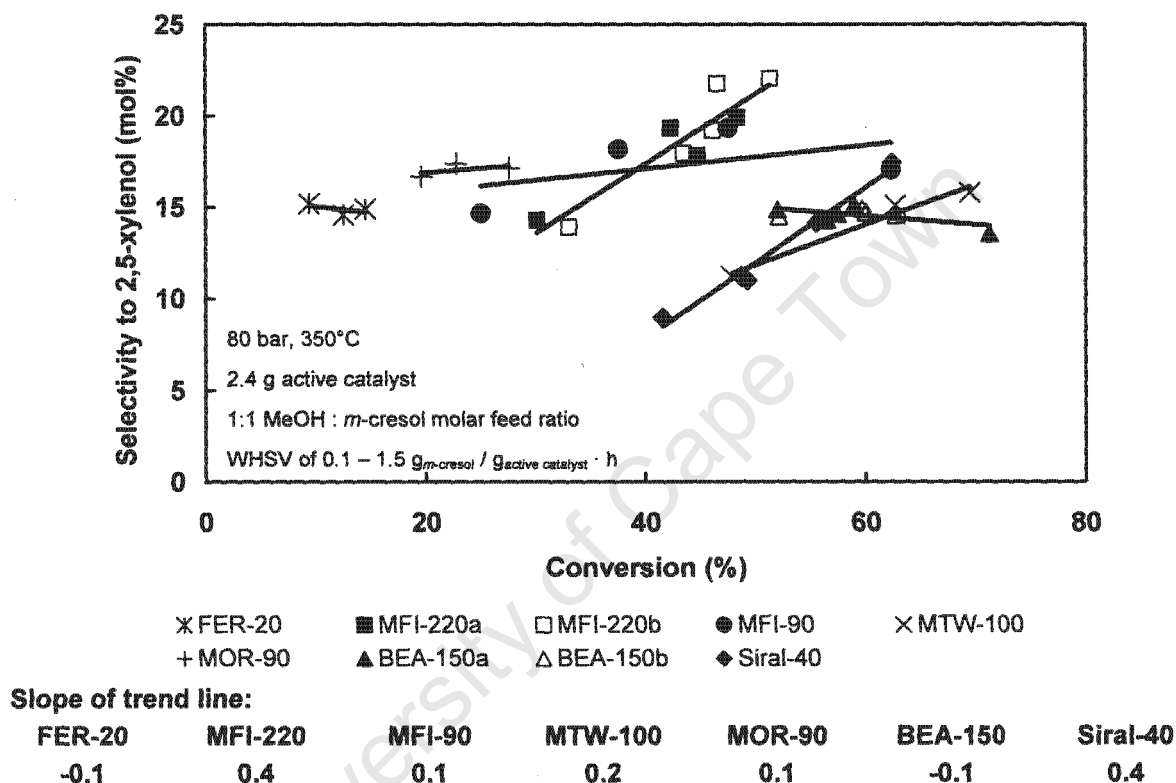


Figure 5-13: Selectivity to 2,5-xylenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.1.2 2,5-Xylenol yield

Figure 5-14 shows that among catalysts tested, medium pore zeolites (FER-20, MFI-90 and MFI-220) and MOR-90, with its unidimensional pore system, yielded higher amounts of 2,5-xylenol as a function of conversion than MTW-100, BEA-150 or Siral-40. All catalysts showed constantly increasing yield of 2,5-xylenol with increasing conversion. There appear to be two “frontiers” designating 2,5-xylenol yield as a function of conversion, one for the medium pore zeolites and MOR-90 that ranges above that of the larger pore zeolites and amorphous Siral-40. The slopes of increase in 2,5-xylenol yield with increasing conversion were similar, ranging between 0.11 and 0.35. Siral-40 and MFI-220 showed the steepest slopes.

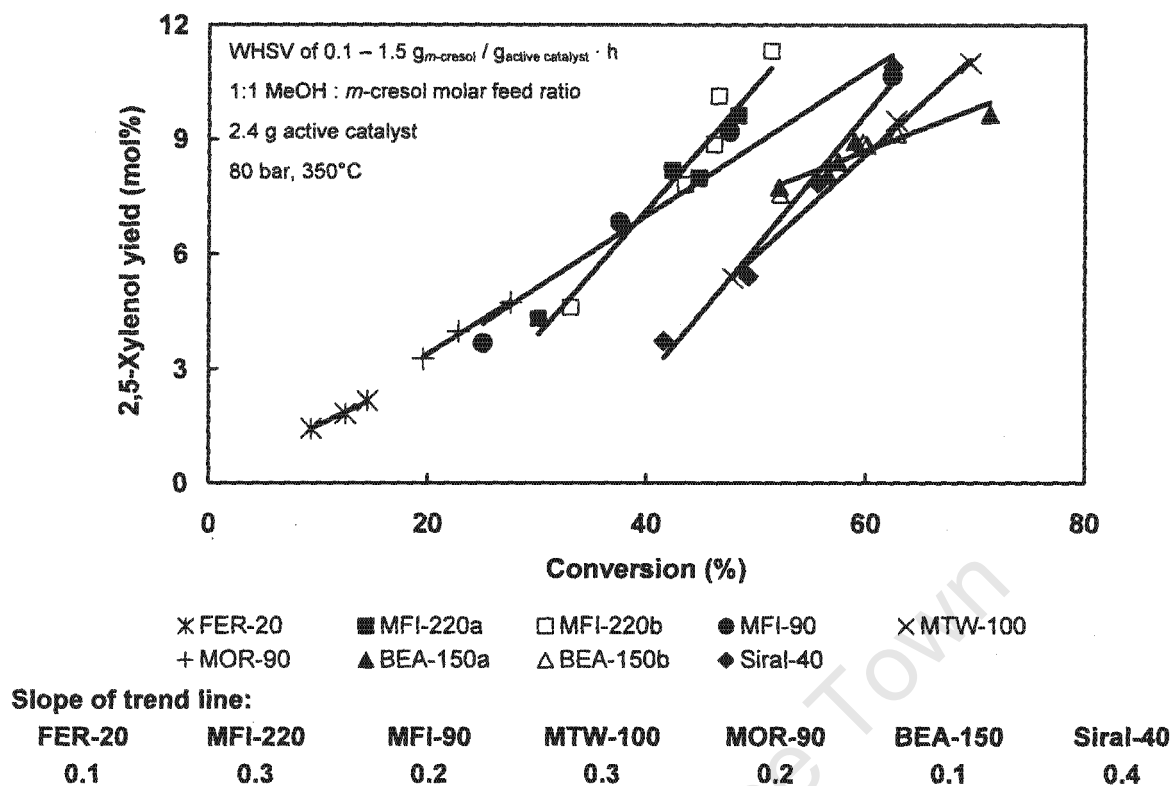


Figure 5-14: 2,5-Xylenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.1.3 Distribution of 2,5-xylenol within phenolic product

FER-20, MOR-90, MFI-220 and Siral-40 produced the highest proportion of 2,5-xylenol within phenolic product (figure 5-15) with MFI-220 and Siral-40 showing similar conversions of between 30 – 65 %. With increasing conversion the proportion of 2,5-xylenol within phenolic product decreased. Apart from MTW-100, the rates of decrease of 2,5-xylenol within phenolic product with conversion of catalysts are similar, ranging between 0.18 and 0.42 mol % (figure 5-15).

Note that the significant differences between selectivities and yields, as shown in figures 5-13 and 5-14, almost disappeared when comparing the percentages of 2,5-xylenol within phenolic product, that is, when 3-methylanisole has been eliminated.

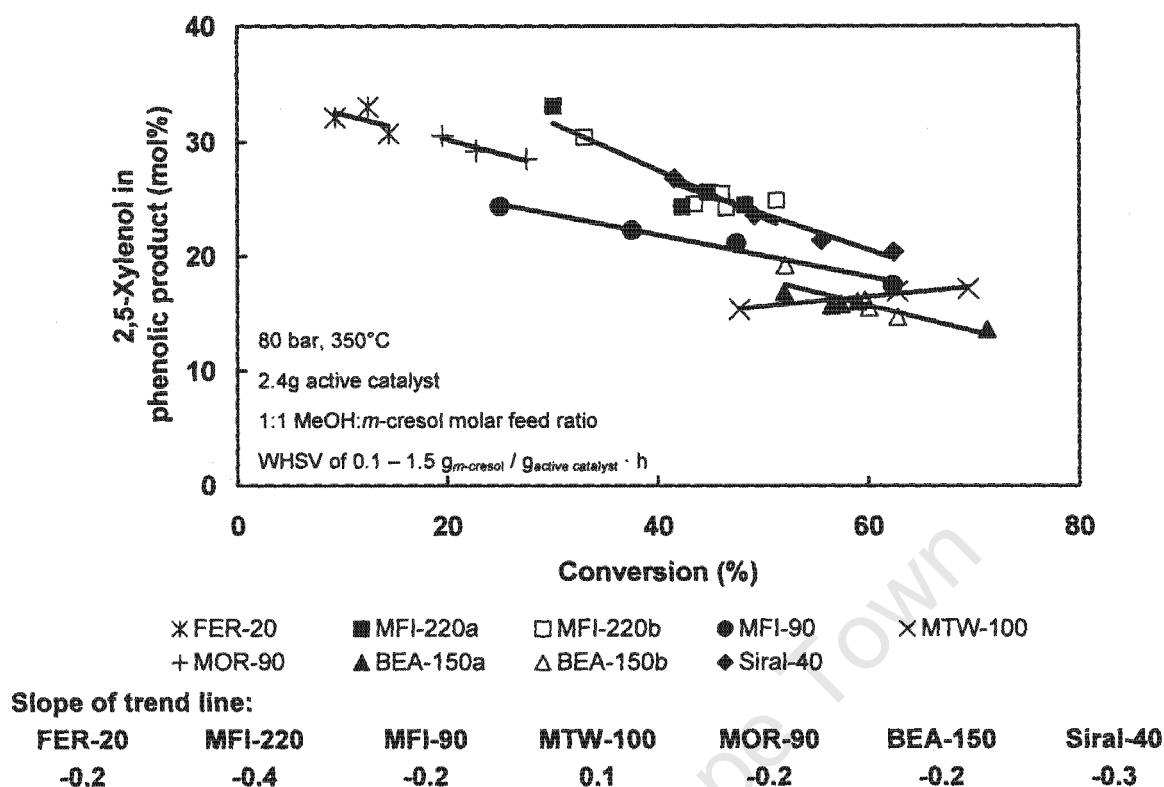


Figure 5-15: Distribution of 2,5-xyleneol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.2 3,4-Xyleneol

5.3.5.2.1 Selectivity of 3,4-xyleneol within product

Selectivity to 3,4-xyleneol varied widely among catalysts tested (figure 5-16). Four catalysts illustrate downward sloping trends, while three show upward sloping trends (within the same range of conversion). Interesting to note is the contrast in trends between MFI-220 (upward sloping) and MFI-90 (downward sloping). Of the tested catalysts, both MFI-90 and MFI-220 showed the highest selectivity to 3,4-xyleneol.

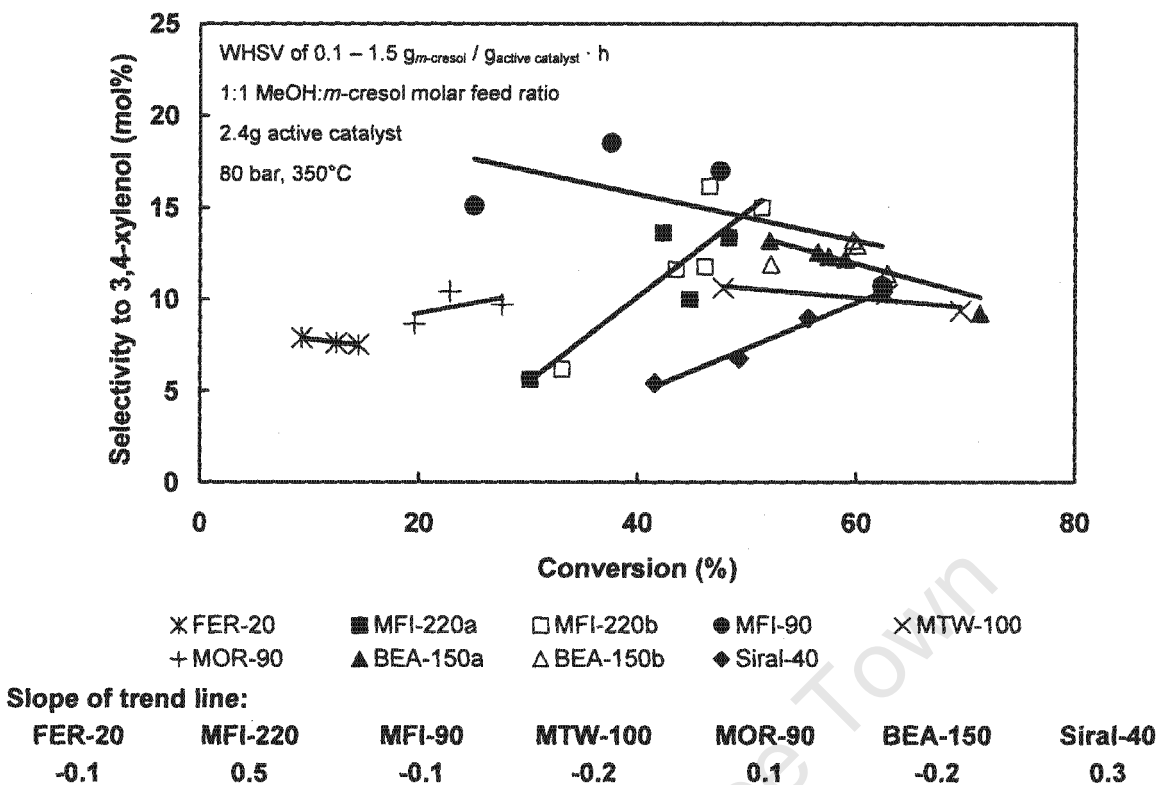


Figure 5-16: Selectivity to 3,4-xyleneol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.2.2 3,4-Xyleneol yield

Between conversions of 45 % and 60 %, MFI-220, MFI-90 and BEA-150 yielded the highest levels of 3,4-xyleneol (figure 5-17). All the catalysts tested show increasing 3,4-xyleneol yield with increasing conversion over the range of conversion achieved. MFI-220 and Siral-40 showed the steepest increase in yield of 3,4-xyleneol as a function of increase in conversion. There is an indication (MFI-90 and BEA-150) that yield of 3,4-xyleneol will pass through a maximum at higher conversion.

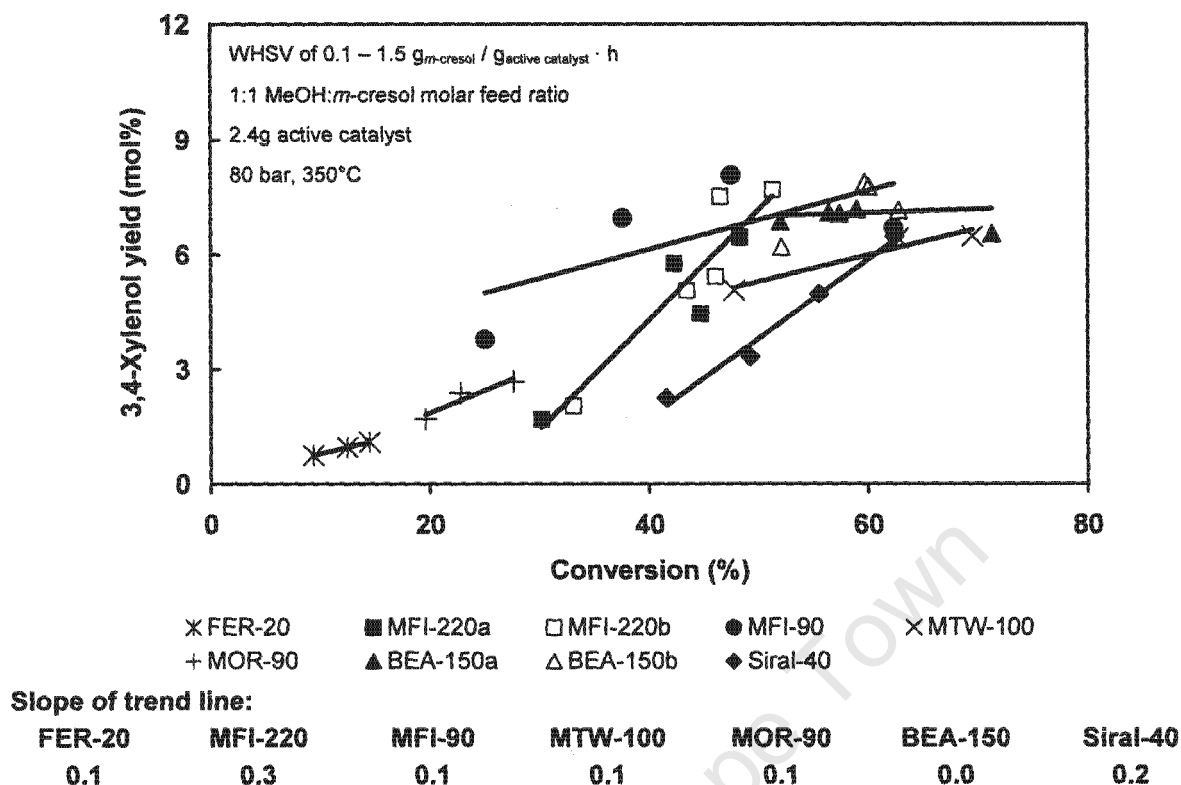


Figure 5-17: 3,4-Xylenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.2.3 Distribution of 3,4-xylenol within phenolic product

Most of the catalysts tested showed decreasing proportion of 3,4-xylenol within phenolic product as conversion increased (figure 5-18). However, MFI-220 shows a different trend. Over MFI-220 the proportion of 3,4-xylenol within phenolic product increased as conversion increased.

The results from catalysts BEA-150, Siral-40, MTW-100 and MFI-90 indicate that a “frontier”, or maximum proportion of 3,4-xylenol within phenolic product may exist. This is illustrated by the converging of trend lines.

As with 2,5-xylenol (see section 5.3.5.1.3 and figure 5-15) the percentages of 3,4-xylenol in phenolic product, for the catalysts tested, are far closer to each other than selectivities and yields.

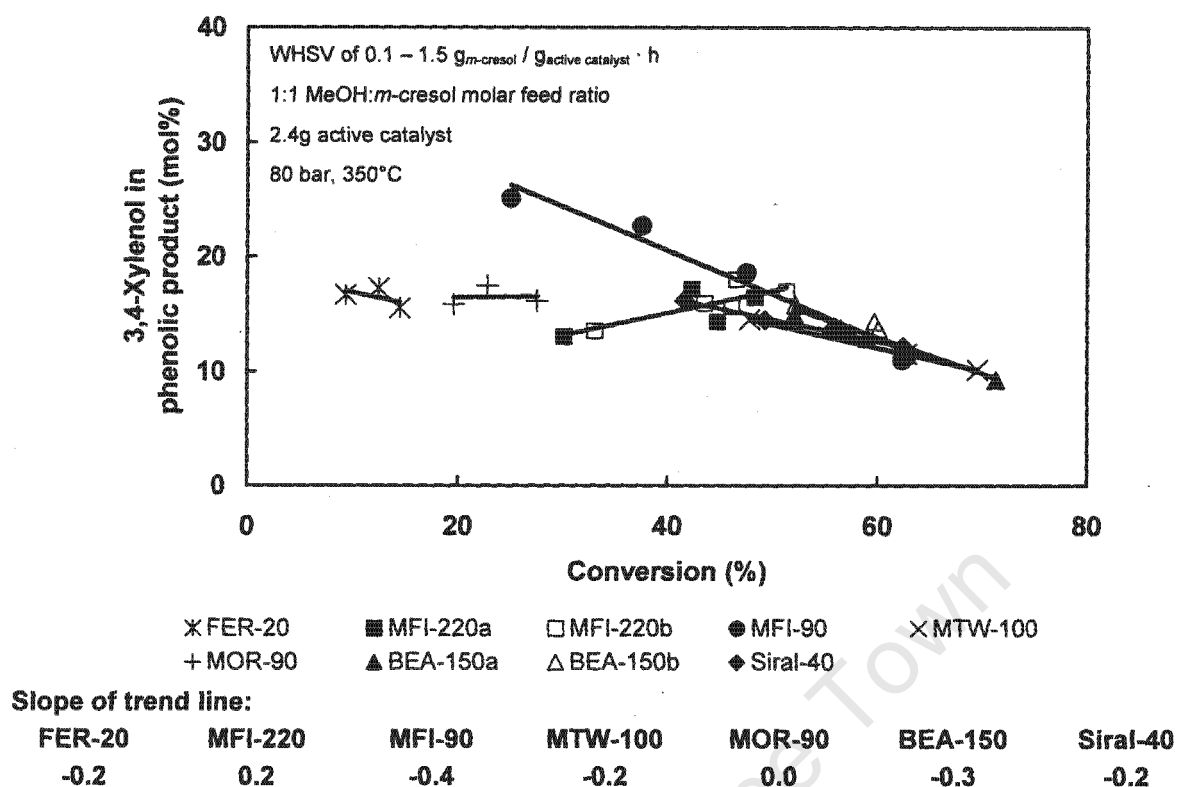


Figure 5-18: Distribution of 3,4-xyleneol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.3 2,3-Xylenol

For the range of conversion achieved, selectivity to 2,3-xylenol ranged between 6 % and 14 % (figure 5-19). There is a clear trend between selectivity to 2,3-xylenol and conversion within this range in that all zeolites showed a decline or at least constancy in selectivity in selectivity (MOR-90) although the average of all data appears to indicate towards a slight increase. However, Siral-40 showed a significant increase in selectivity with increasing conversion. The zeolite with the largest pores, BEA-150 and amorphous Siral-40 showed highest selectivities. Smaller or unidimensional pore zeolites, FER-20, MFI-90, MFI-220 and MOR-90 showed lower levels of selectivity to 2,3-xylenol.

Over all catalysts tested, yield of 2,3-xylenol increased with increasing conversion (figure 5-20). However, at higher conversion differences were significant. BEA-150 and Siral-40 yielded more 2,3-xylenol than the other catalysts. The outlier, shown in brackets (achieved over BEA-150) was ignored. Siral-40 shows the steepest increase in 2,3-xylenol yield with increasing conversion. MFI-90 and MFI-220 portray very similar trends although MFI-220 experienced a slightly higher increase. As for selectivities, differences are much more pronounced at high conversions.

All catalysts tested showed decreasing proportions of 2,3-xyleneol within phenolic product for increasing conversion, but again with significant differences (figure 5-21). MFI-220 experienced the steepest decline, while FER-20 experienced the smallest decline.

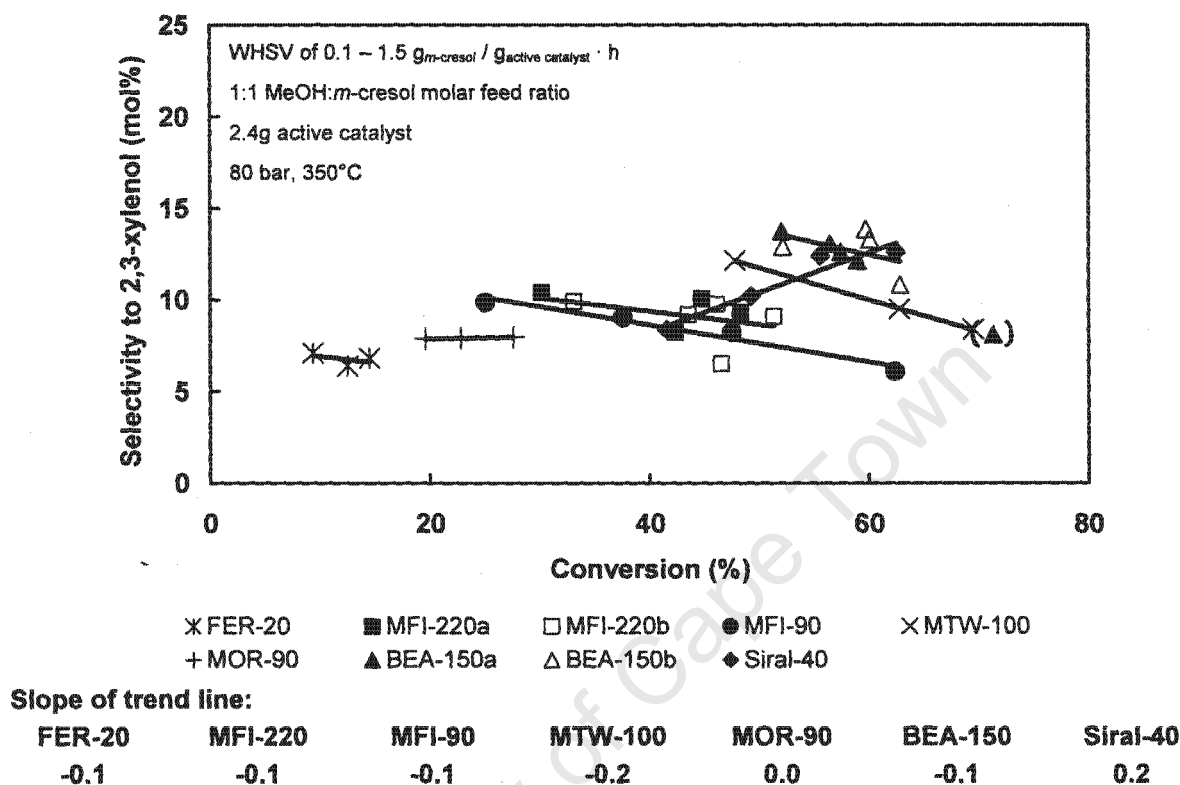


Figure 5-19: Selectivity to 2,3-xyleneol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

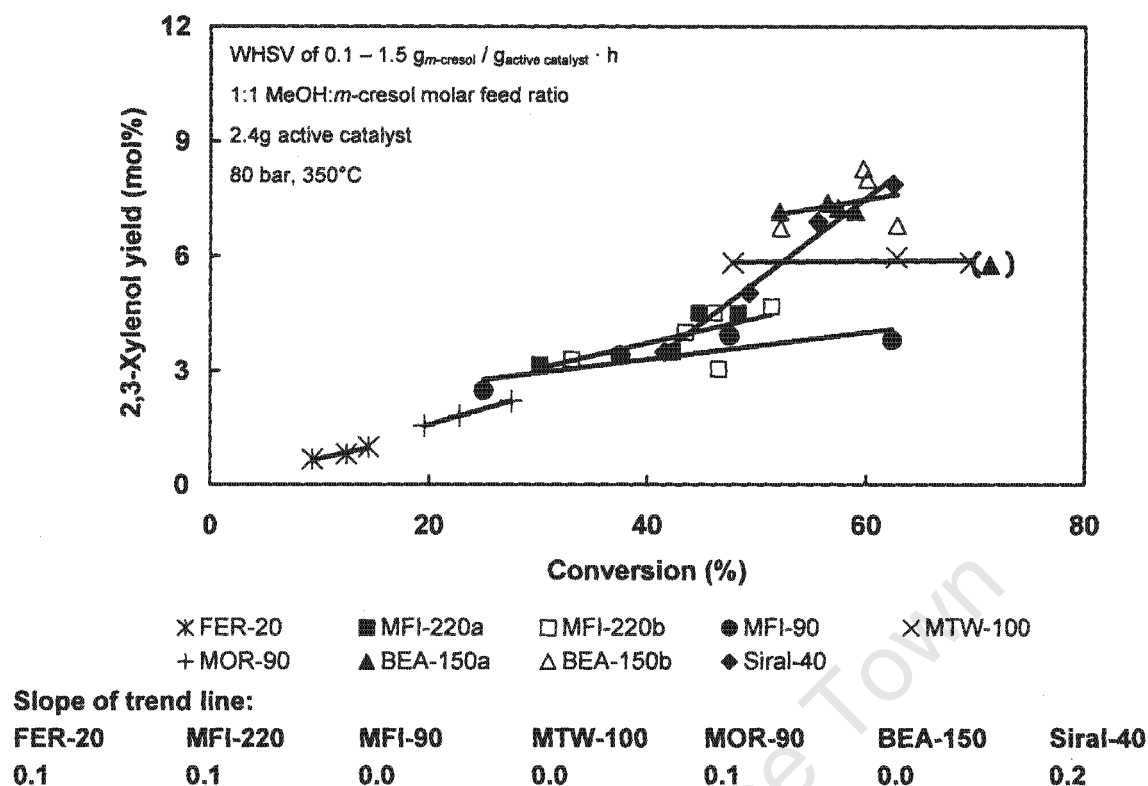


Figure 5-20: 2,3-Xylenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

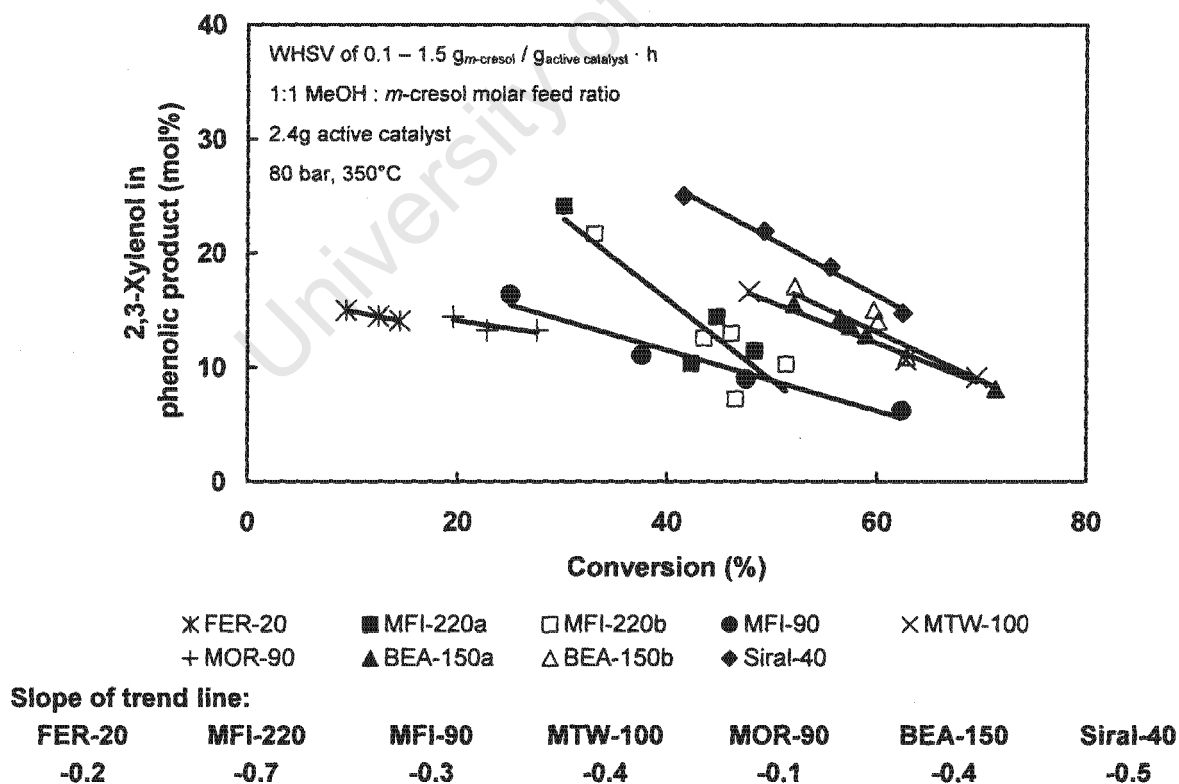


Figure 5-21: Distribution to 2,3-xylenol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.4 3,5-Xylenol

BEA-150 and MTW-100 produced the highest selectivity to 3,5-xylenol, with over 2 % 3,5-xylenol being produced over BEA-150 at conversion of 71 % (figure 5-23). Comparatively the lowest selectivity to 3,5-xylenol, at high conversion, was produced over Siral-40. Over FER-20 and MOR-90 very little 3,5-xylenol was produced, however, this was at rather low levels of conversion. Over the other catalysts, selectivities to 3,5-xylenol were small. The selectivity to 3,5-xylenol increased greatly with increasing conversion.

Correspondingly practically no 3,5-xylenol was produced at low conversion (figure 5-23). Above conversion of approximately 50 % 3,5-xylenol yield began to increase. The largest amount of 3,5-xylenol (2.2 %) was yielded at 71 % conversion over BEA-150.

The proportion of 3,5-xylenol within the phenolic product was also low over all catalysts but increased with increasing conversion (figure 5-24).

In every regard, be it selectivity, yield or percentage in the phenolic product, the same trend was observed, namely no 3,5-xylenol formed up to around 50 % conversion. Thereafter the abundance of 3,5-xylenol increased significantly, though still on low, but similar levels for all the catalysts tested (figures 5-22 to 5-24).

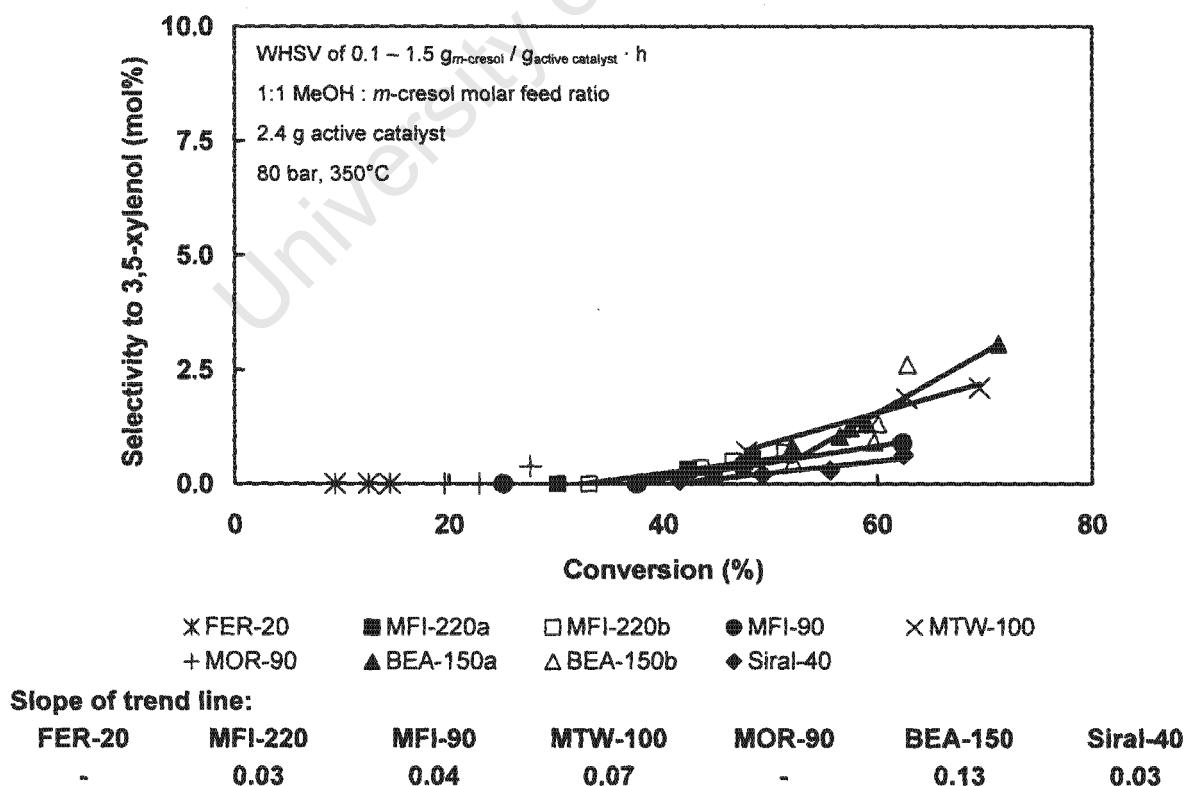


Figure 5-22: Selectivity to 3,5-xylenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

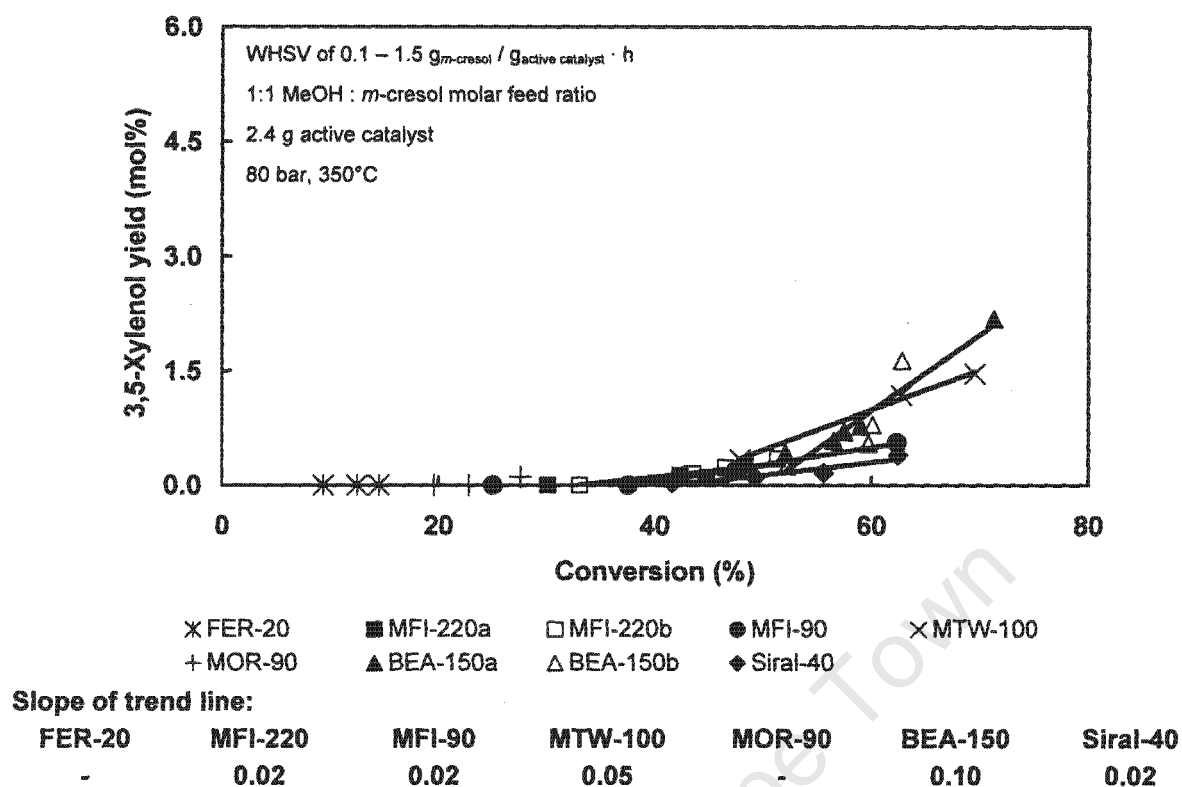


Figure 5-23: 3,5-Xylenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

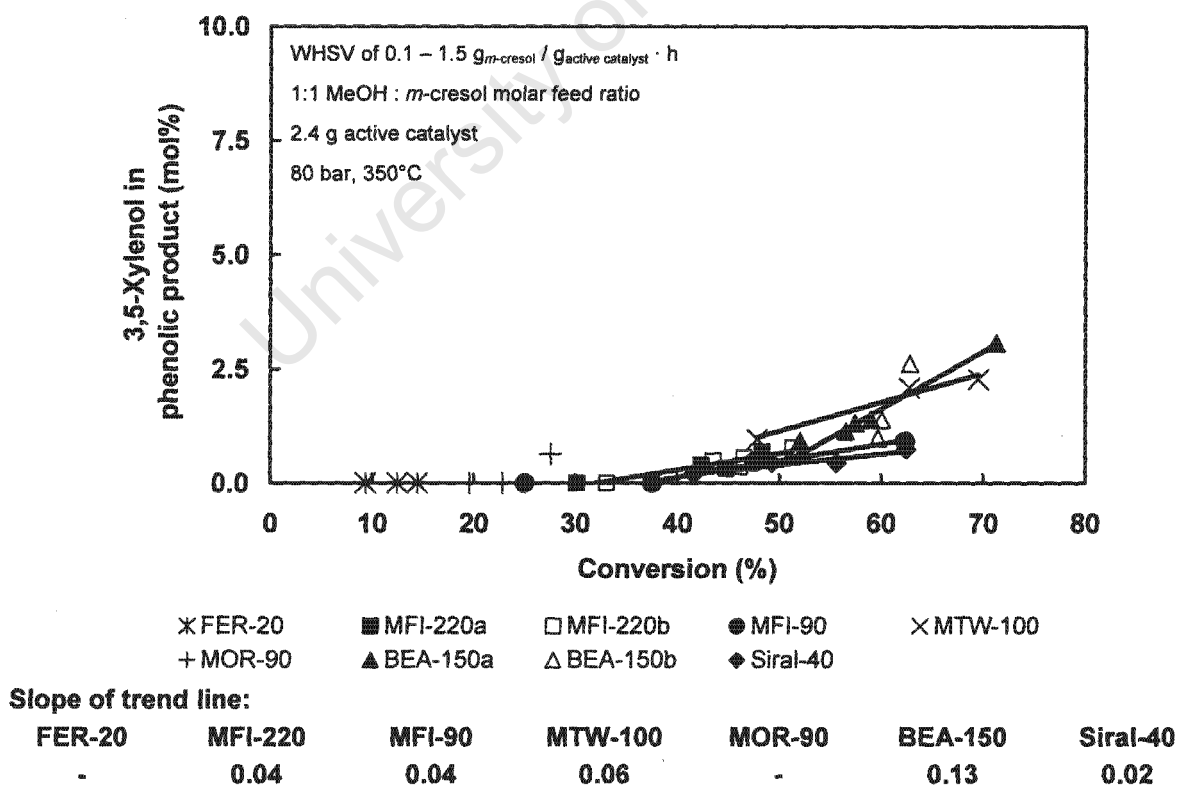


Figure 5-24: Distribution to 3,5-xylenol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.5 2,4-Xylenol

2,4-xylenol was produced at highest selectivity of 9.1 % over MFI-90 at a conversion of 62 % (figure 5-25). BEA-150 also produced 2,4-xylenol at relatively high selectivities. Selectivity to 2,4-xylenol increased steeply over both MFI-90 and BEA-150. Lower selectivities were observed over MFI-220 and MTW-100.

A maximum of 5.6 mol % 2,4-xylenol was yielded over MFI-90. Very small amounts of 2,4-xylenol was yielded over Siral-40 while practically no 2,4-xylenol was yielded over MOR-90 or FER-20 (figure 5-26). All yields increased, although comparatively more steeply over MFI-90 and BEA-150.

The highest proportion of 2,4-xylenol within phenolic product (9.3 %) was produced over MFI-90 (figure 5-27). In general, proportions of 2,4-xylenol increased rather steeply with increasing conversion.

All catalysts showed increasing selectivity, yield and proportions of 2,4-xylenol within phenolic product with increasing levels of conversion (figures 5-25 to 5-27). However, the differences in magnitude between each of these catalysts were large.

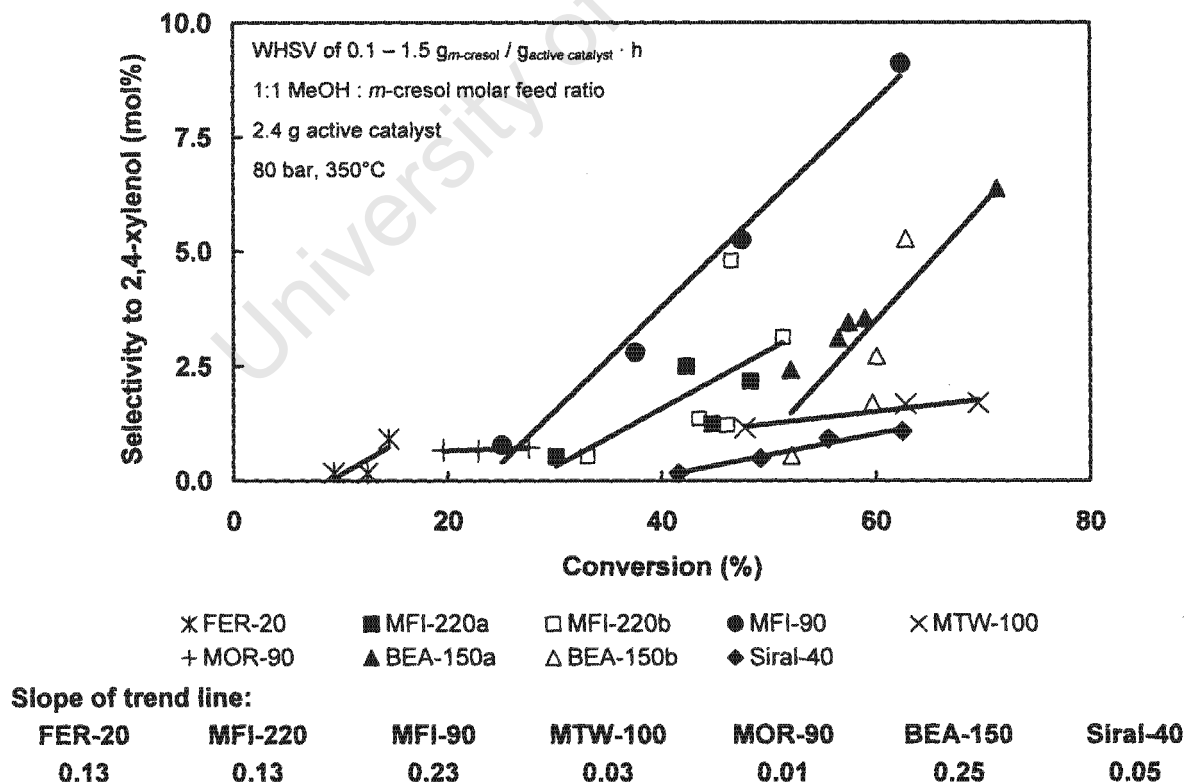


Figure 5-25: Selectivity to 2,4-xylenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

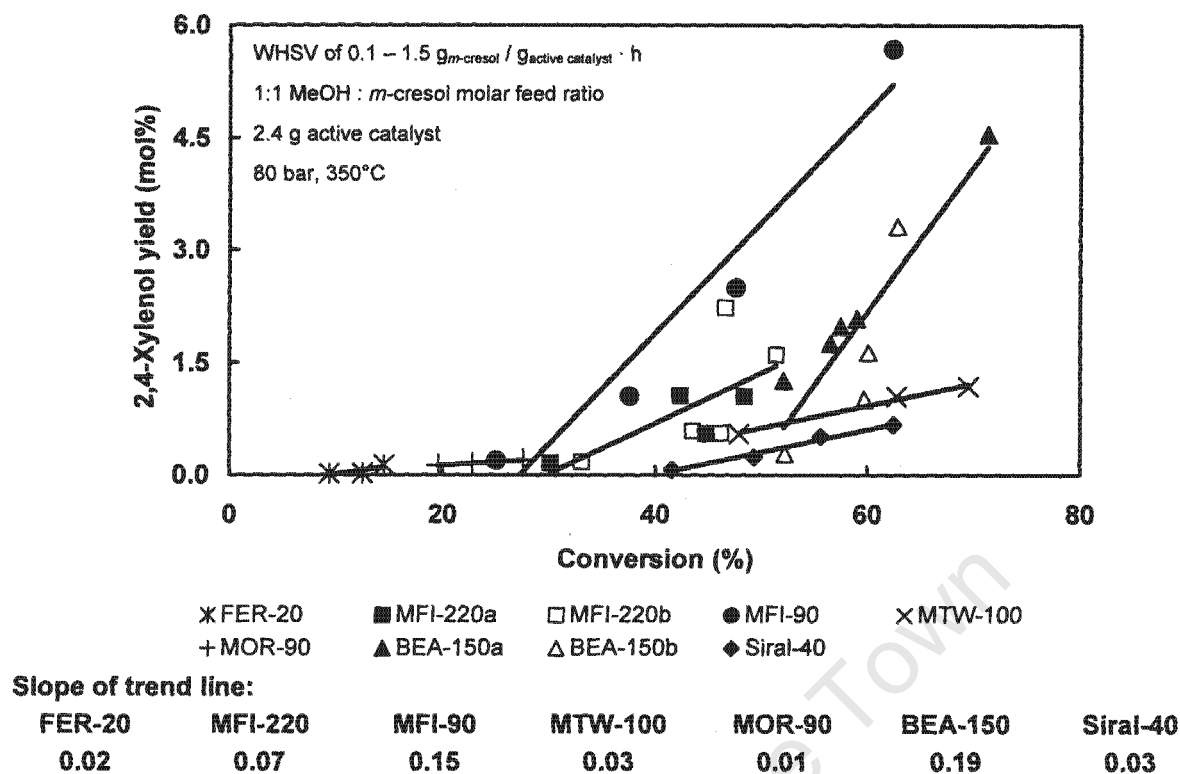


Figure 5-26: 2,3-Xylenol yield versus *m*-cresol conversion
for *m*-cresol methylation over catalysts tested

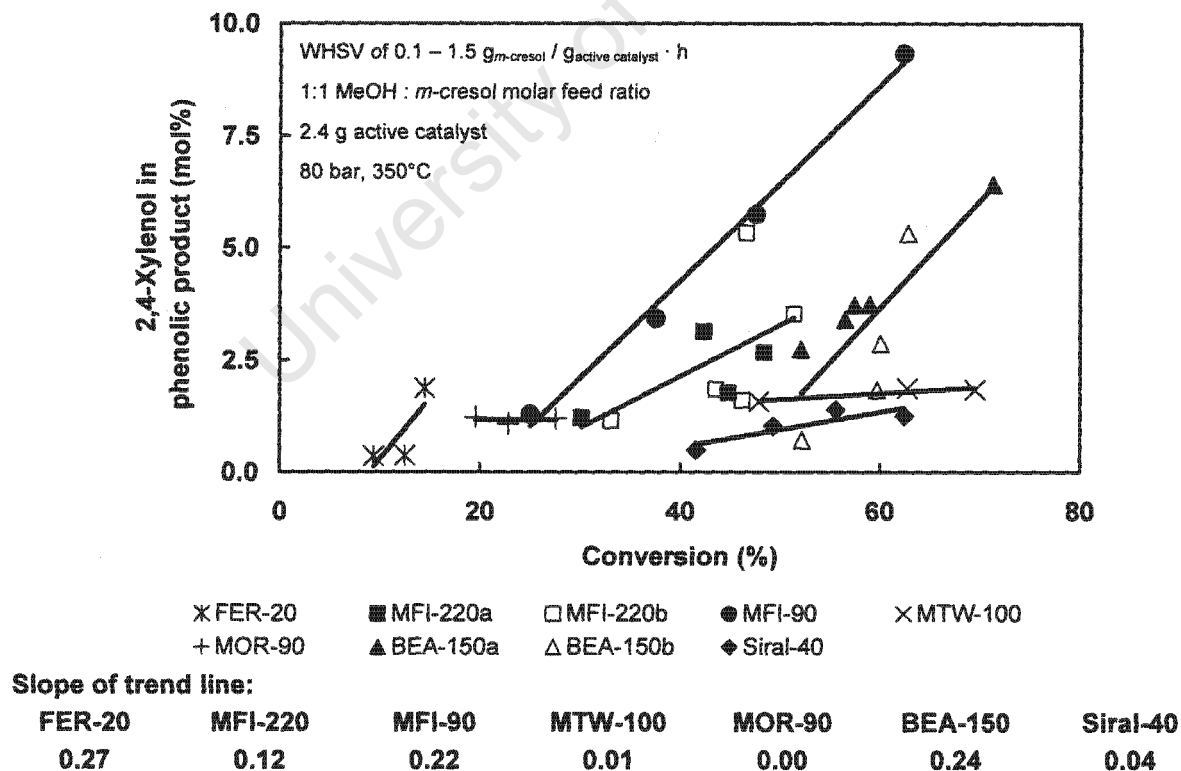


Figure 5-27: Distribution to 2,3-xylenol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.5.6 2,6-Xylenol

Selectivity to, yield of and percentage in phenolic product of 2,6-xylenol was low over all catalysts tested (figures 5-28 to 5-30). Catalysts MFI-90, MFI-220 and BEA-150 showed reasonable increases in yield as conversion increased (figure 5-29). Highest yields of 2,6-xylenol were seen over MFI-90 and BEA-150.

FER-20 and MOR-90, over which low conversions were achieved, yielded practically no 2,6-xylenol at all. Relatively low but constant yields (>0.25 mol %) were achieved over Siral-40. MTW-100 and Siral-40 showed declining trends that were very different to those seen over the other catalysts.

MFI-90 showed the highest percentage of 2,4-xylenol within the phenolic product (approximately 2 mol %, in figure 5-30). Percentages over the other catalysts were slightly lower. In general, the percentage of 2,4-xylenol within phenolic product was low over all catalysts tested.

Over all catalysts tested, formation of 2,6-xylenol occurred only at about 30 % conversion and higher but remained low in every regard (figures 5-28 to 5-30).

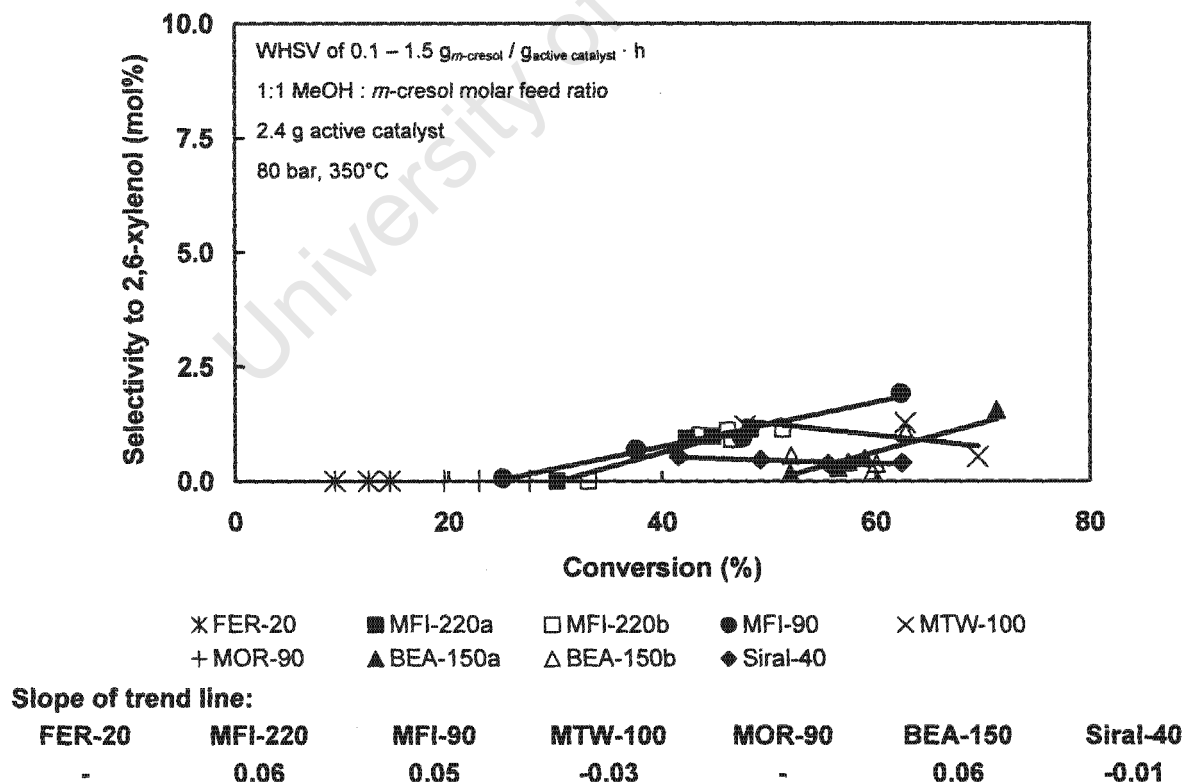


Figure 5-28: Selectivity to 2,6-xylenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

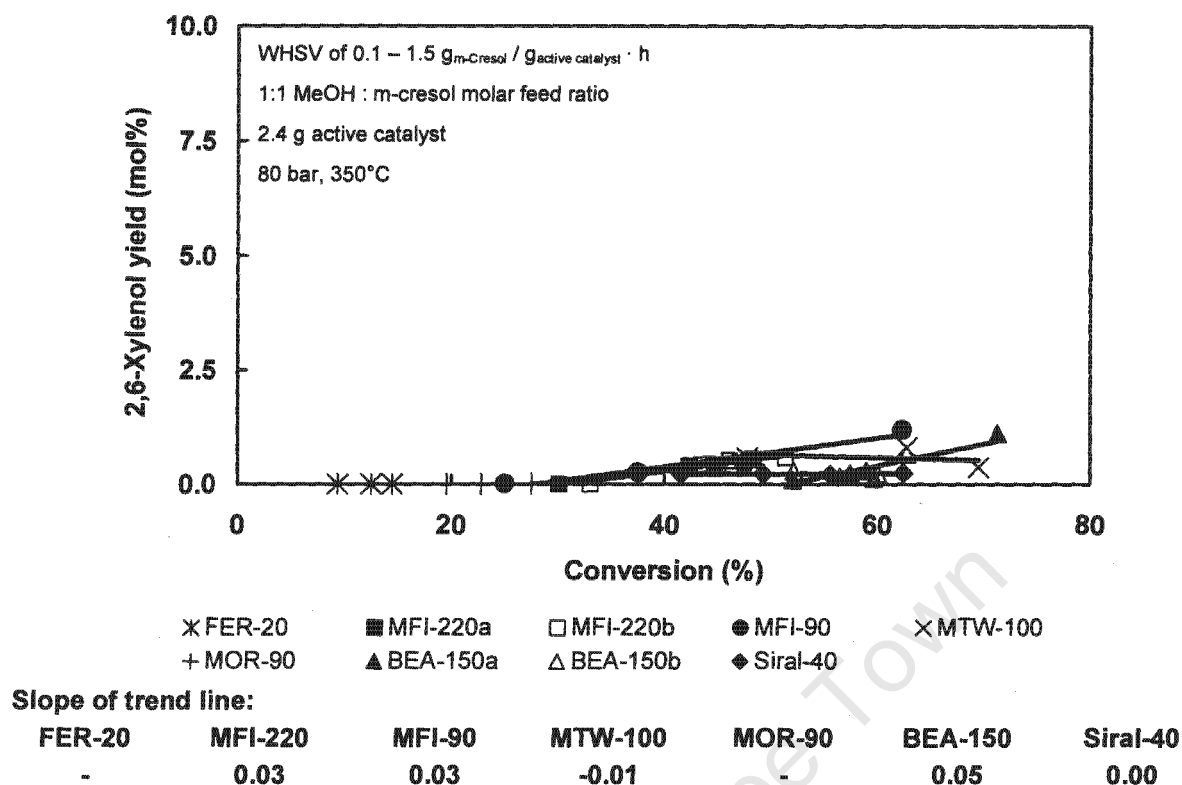


Figure 5-29: 2,4-Xylenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

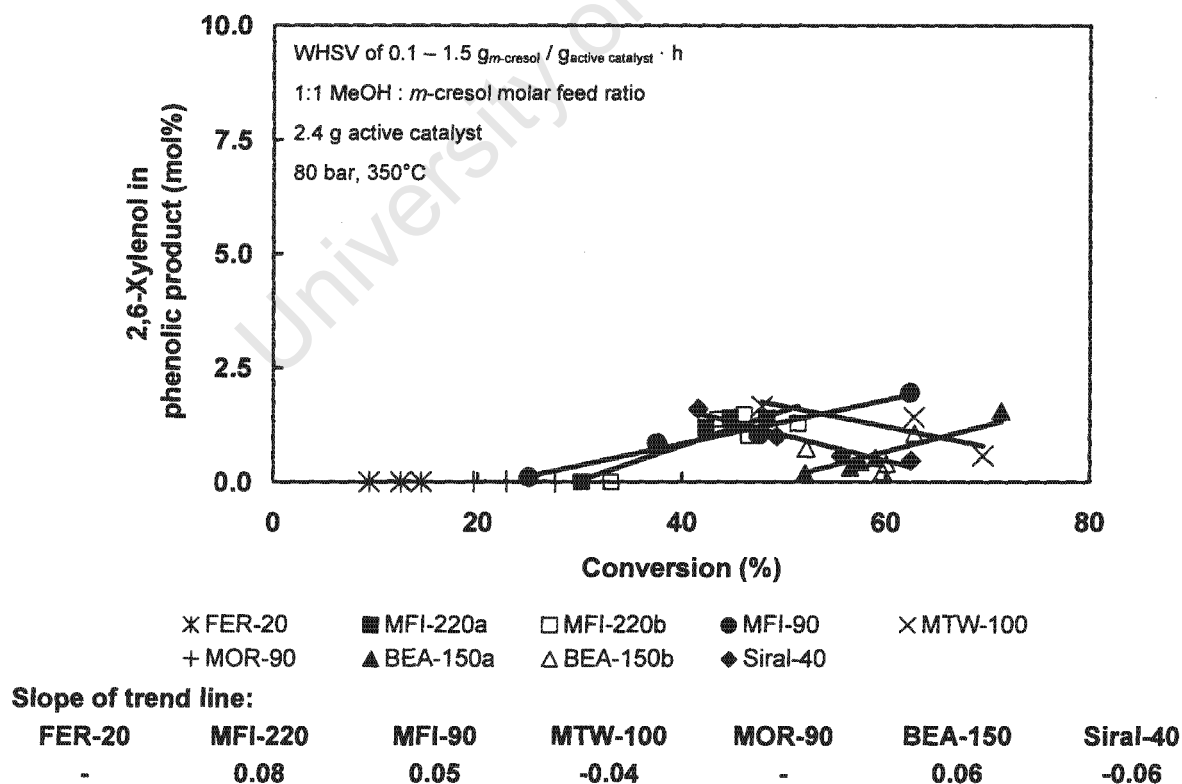


Figure 5-30: Distribution to 2,6-xylenol within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.6 Trimethylphenols (TMPs)

Trimethylphenols (TMPs) were often present in products. These were produced as by-products in the methylation of *m*-cresol to xylenols. 2,4,5-Trimethylphenol was the most abundant isomer, followed by 2,3,5-, 2,3,6-, 2,3,4-, 3,4,5- and 2,4,6-TMP isomers respectively. Highest levels of TMPs were observed over BEA-150 and MTW-100. Siral-40 produced the lowest levels of TMPs.

Selectivity to TMPs generally increased with increasing conversion (see figure 5-31). This is particularly evident for conversion of above 30 %. For conversions of between 30 % and 70 % all the catalysts showed similar behaviour, with trend line slopes close to 0.5. BEA-150 produced TMPs at the highest selectivity of 28 % at a conversion of 71 %. At a comparative level of conversion, 62 %, Siral-40 produced TMPs at the lower selectivity of 15 %, although the slope of increase in selectivity to TMPs with increasing conversion was similar to that observed over the zeolites.

TMP yields are shown in figure 5-32 and the proportions of TMPs in the phenolic product are shown in figure 5-33. BEA-150 and MTW-100 produced relatively high amounts (up to 28 %) of trimethylphenols within the phenolic product. The proportions of TMPs in phenolic product show trends are similar to the trends in selectivity.

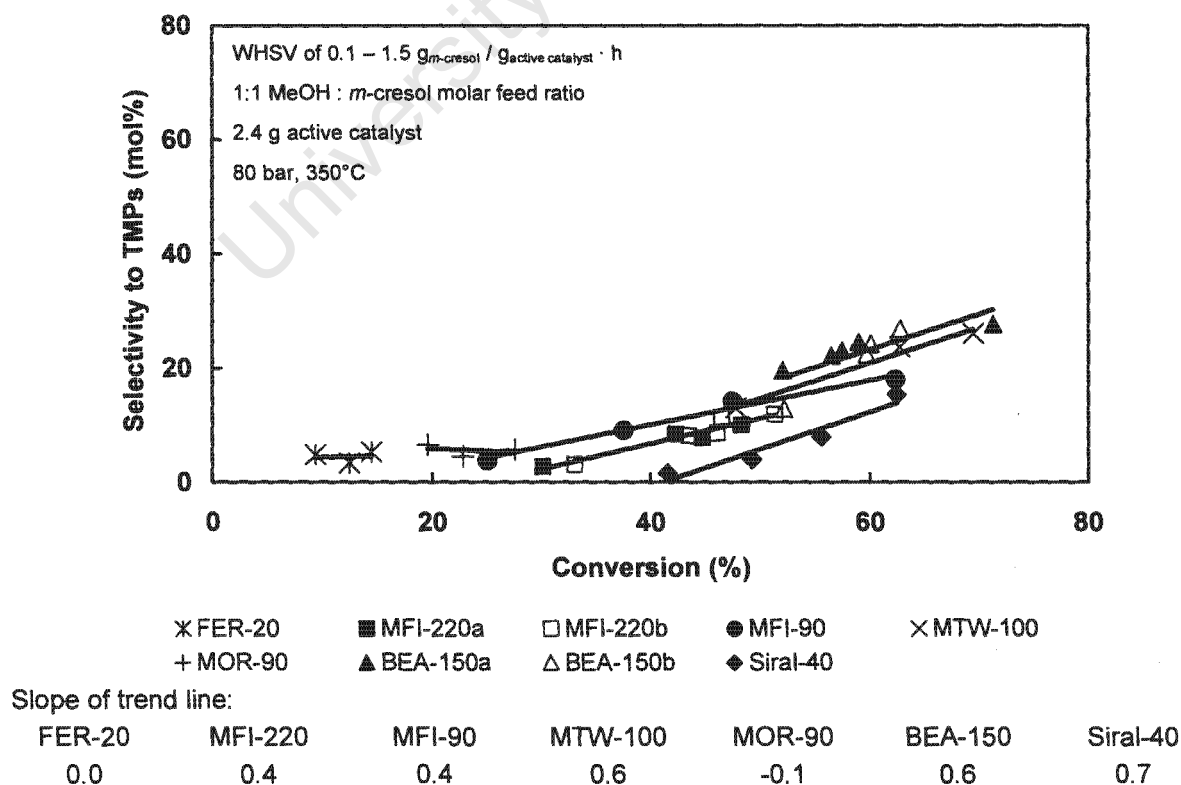


Figure 5-31: Selectivity to trimethylphenols (TMPs) versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

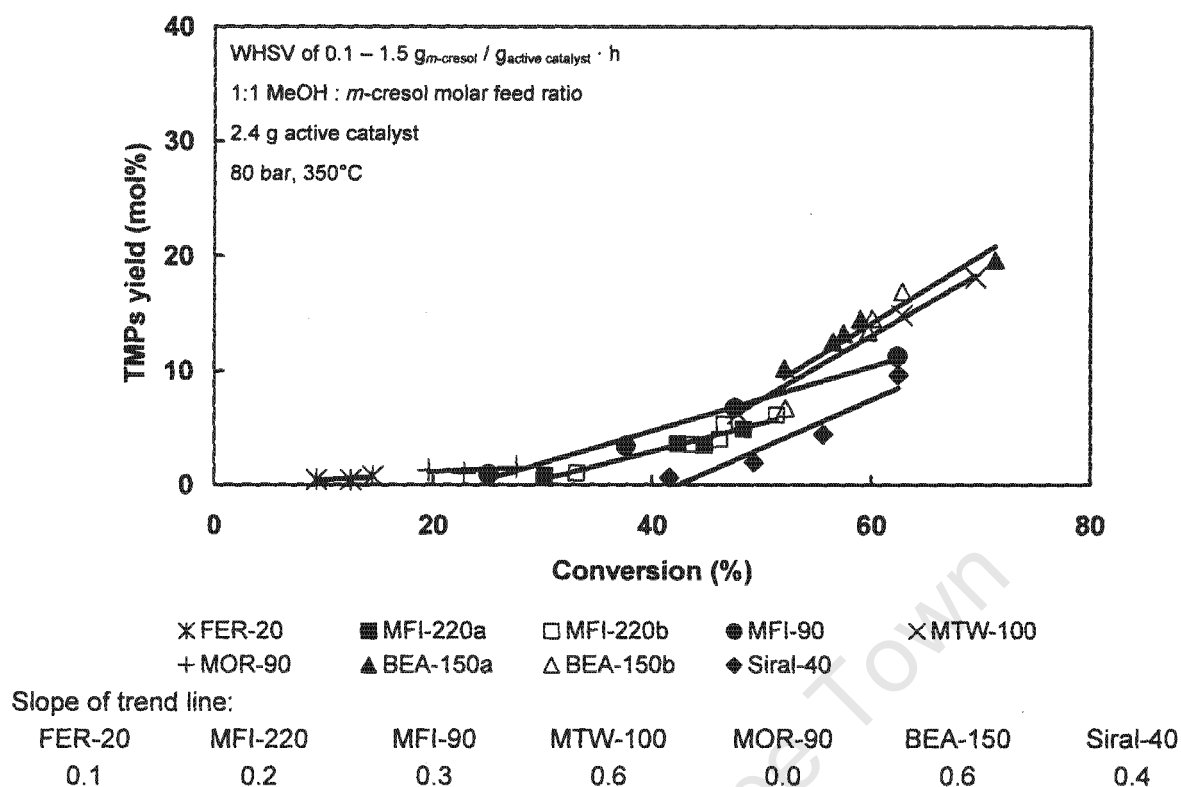


Figure 5-32: Trimethylphenols (TMPs) yield versus *m*-cresol conversion for *m*-cresol methylation for catalysts tested

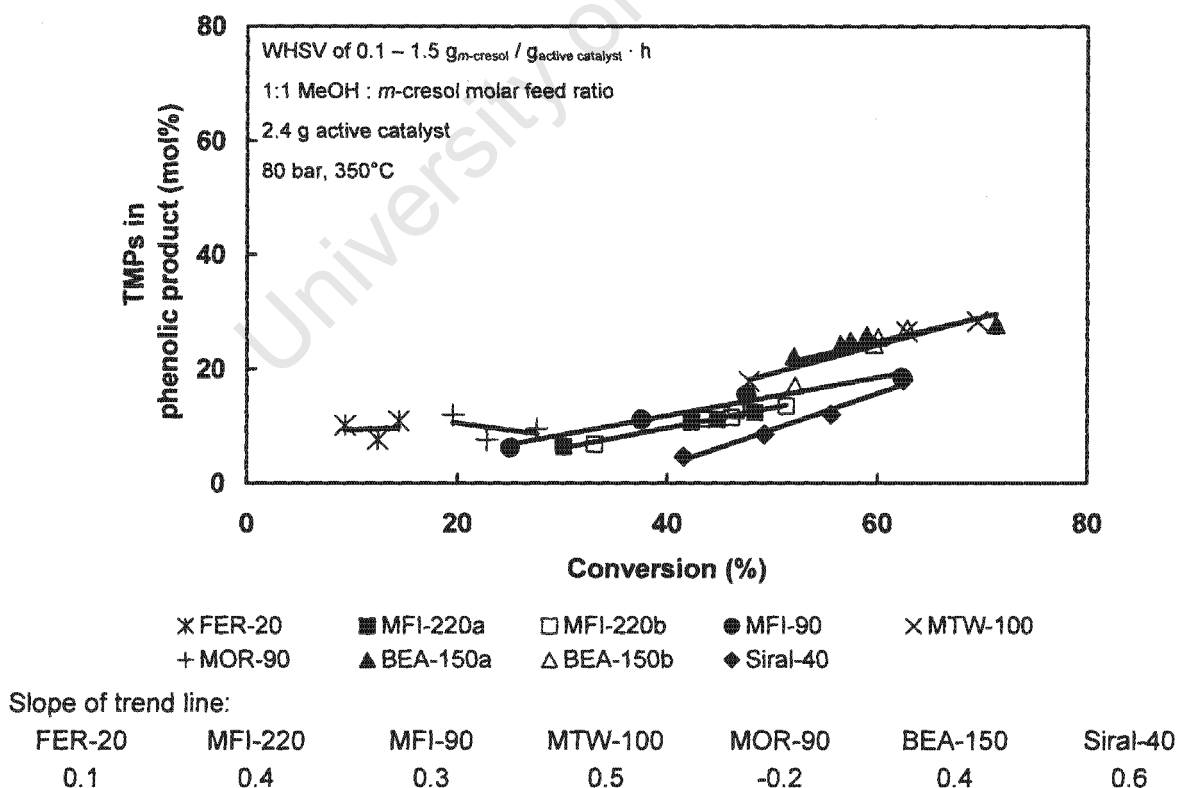


Figure 5-33: Distribution to trimethylphenols (TMPs) within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7 Individual trimethylphenol (TMP) Isomers

Note that slopes of all curves of selectivities and yields in figures 5-34 to 5-45 are positive (exceptions are due to significant data scatter) particularly at higher conversions. Therefore slopes are not given in these figures.

5.3.7.1 Selectivity to and yield of 2,3,4-trimethylphenol

Figures 5-34 and 5-35 show the selectivity to and yield, respectively, of 2,3,4-trimethylphenol achieved over the catalysts tested.

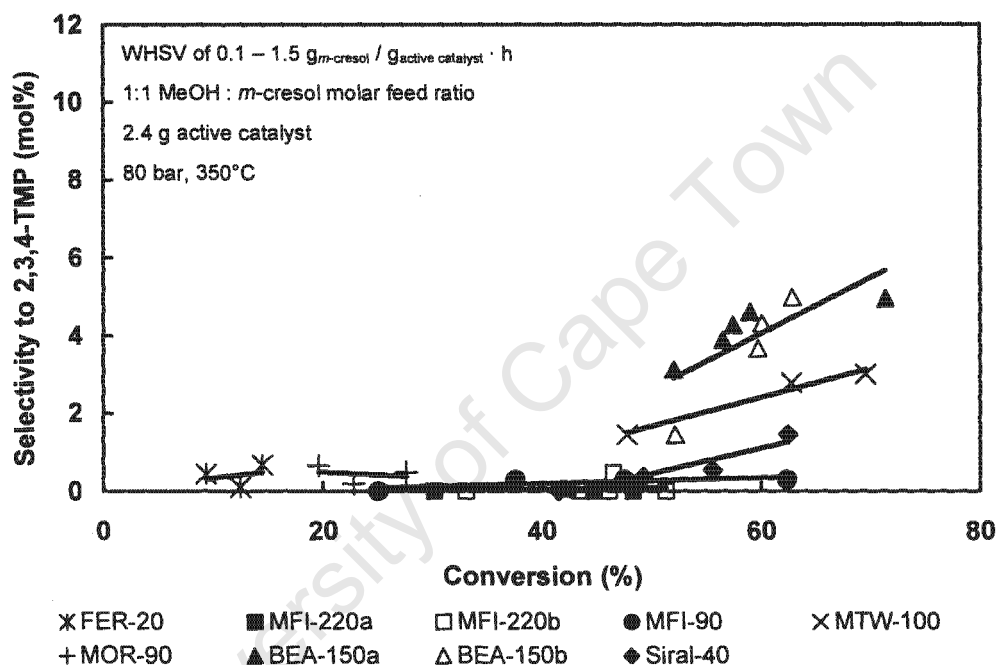


Figure 5-34: Selectivity to 2,3,4-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

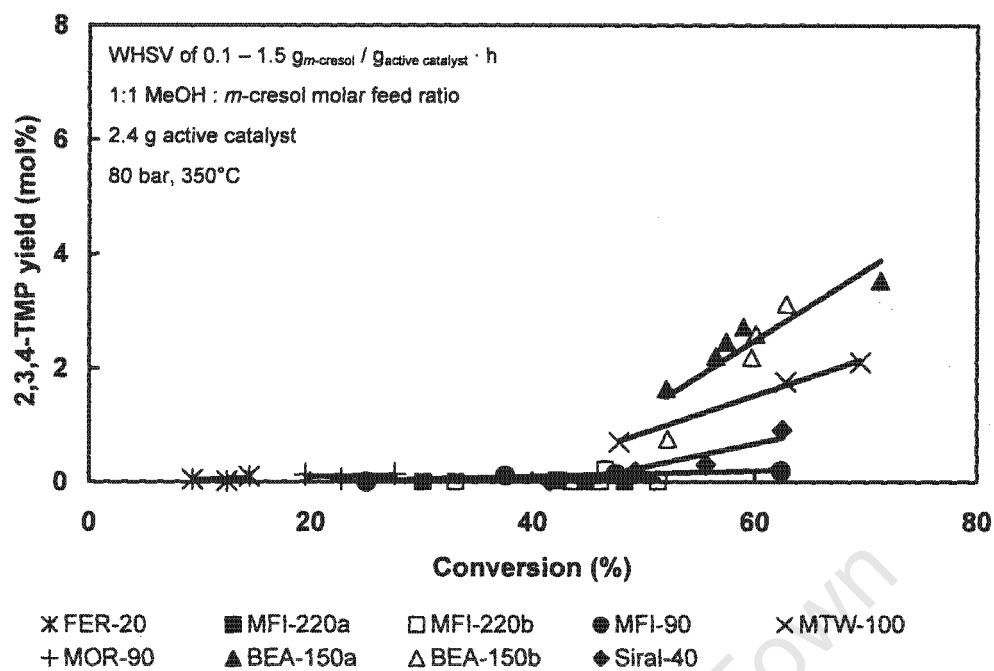


Figure 5-35: 2,3,4-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.2 Selectivity to and yield of 2,3,5-trimethylphenol

Figures 5-36 and 5-37 show the selectivity to and yield, respectively, of 2,3,5-trimethylphenol achieved over the catalysts tested.

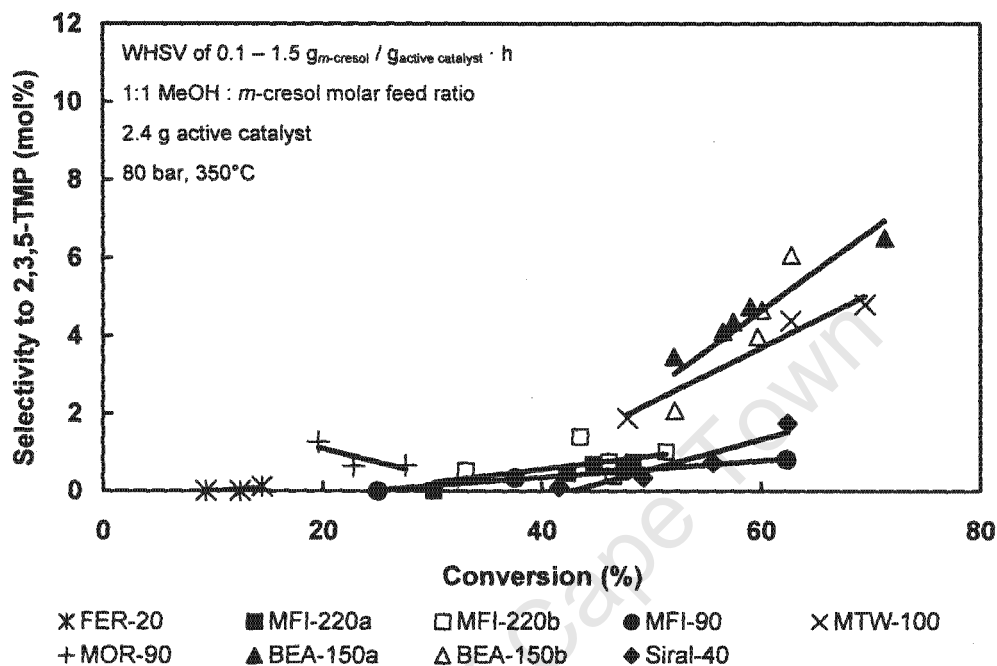


Figure 5-36: Selectivity to 2,3,5-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

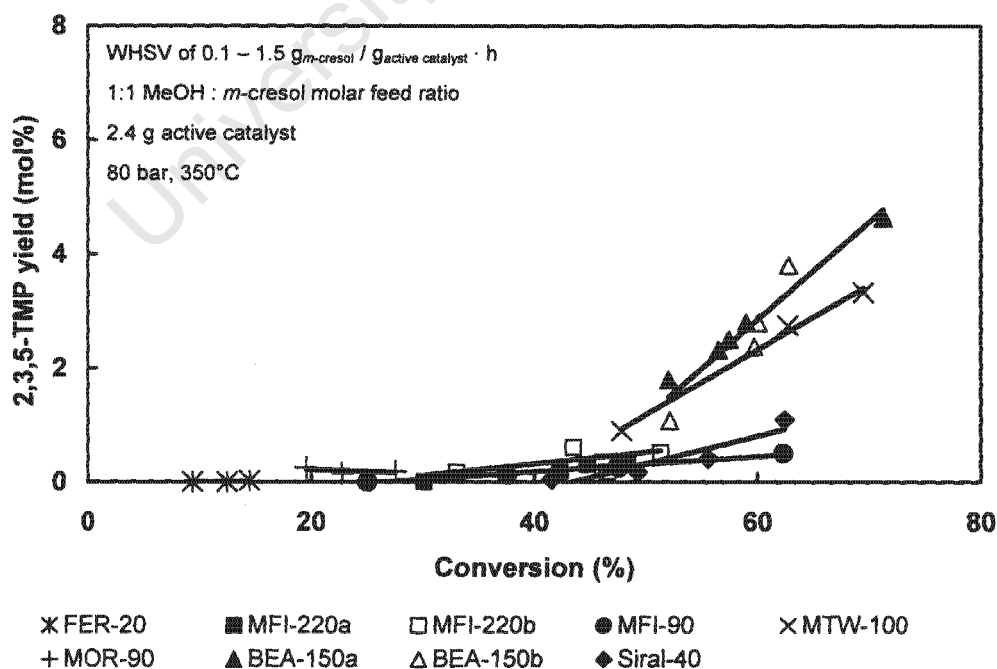


Figure 5-37: 2,3,5-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.3 Selectivity to and yield of 2,3,6-trimethylphenol

Figures 5-38 and 5-39 show the selectivity to and yield, respectively, of 2,3,6-trimethylphenol achieved over the catalysts tested.

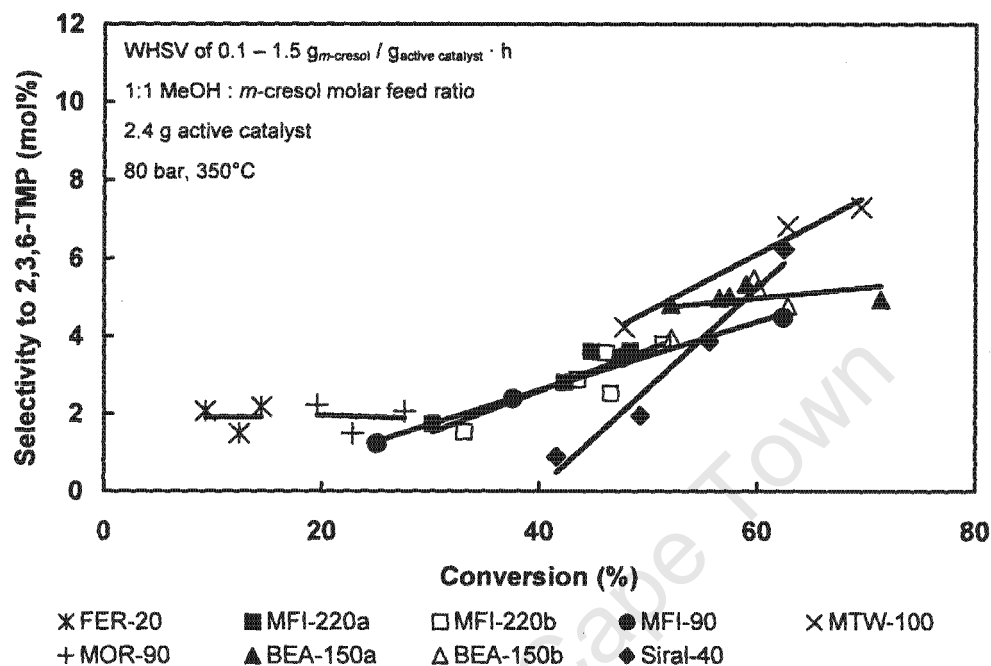


Figure 5-38: Selectivity to 2,3,6-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

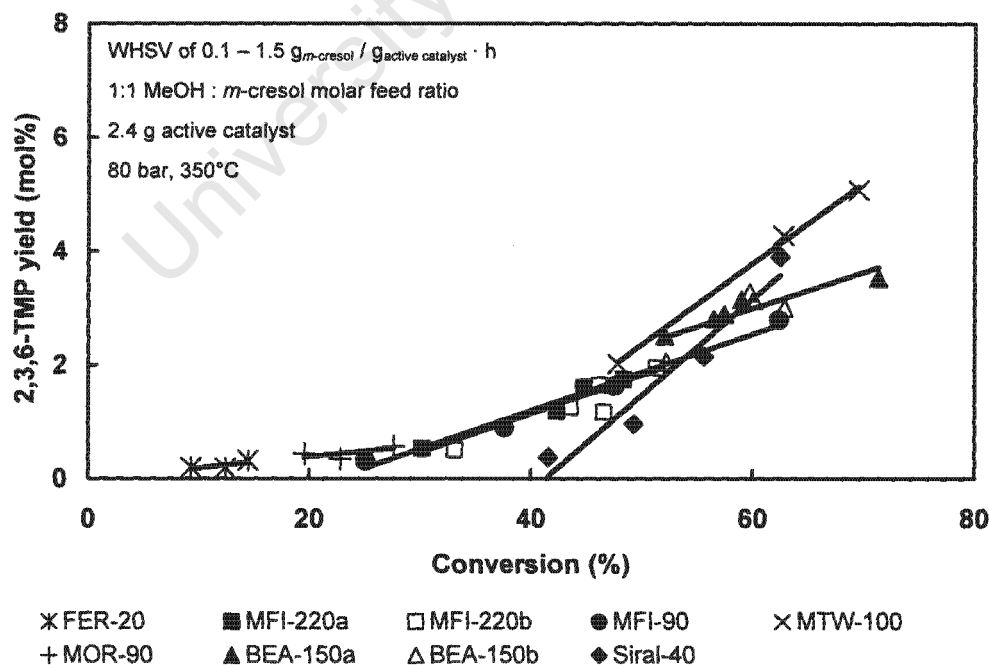


Figure 5-39: 2,3,6-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.4 Selectivity to and yield of 2,4,5-trimethylphenol

Figures 5-40 and 5-41 show the selectivity to and yield, respectively, of 2,4,5-trimethylphenol achieved over the catalysts tested.

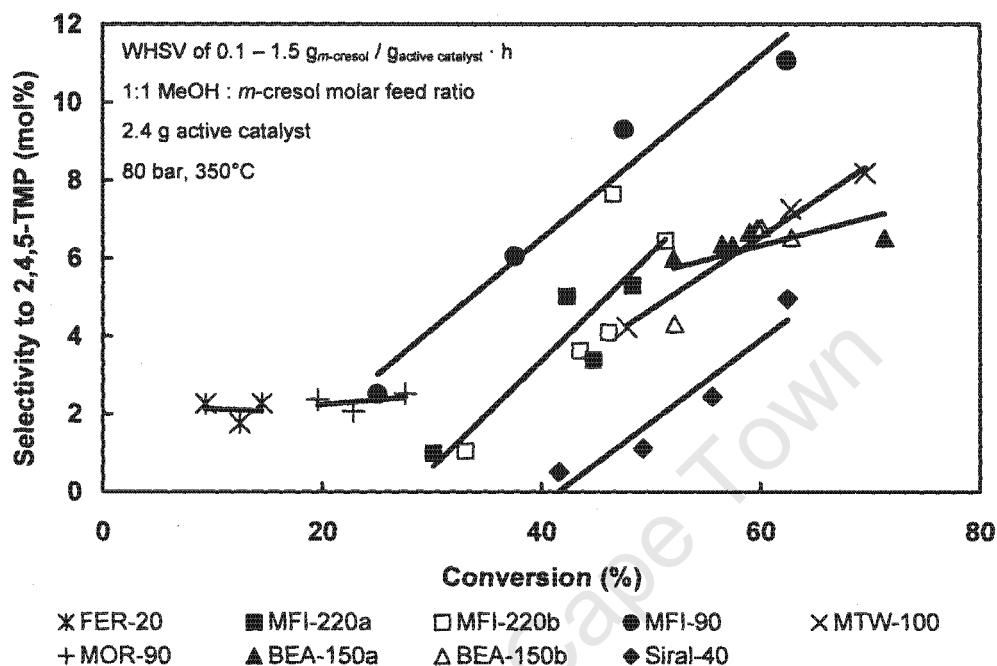


Figure 5-40: Selectivity to 2,4,5-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

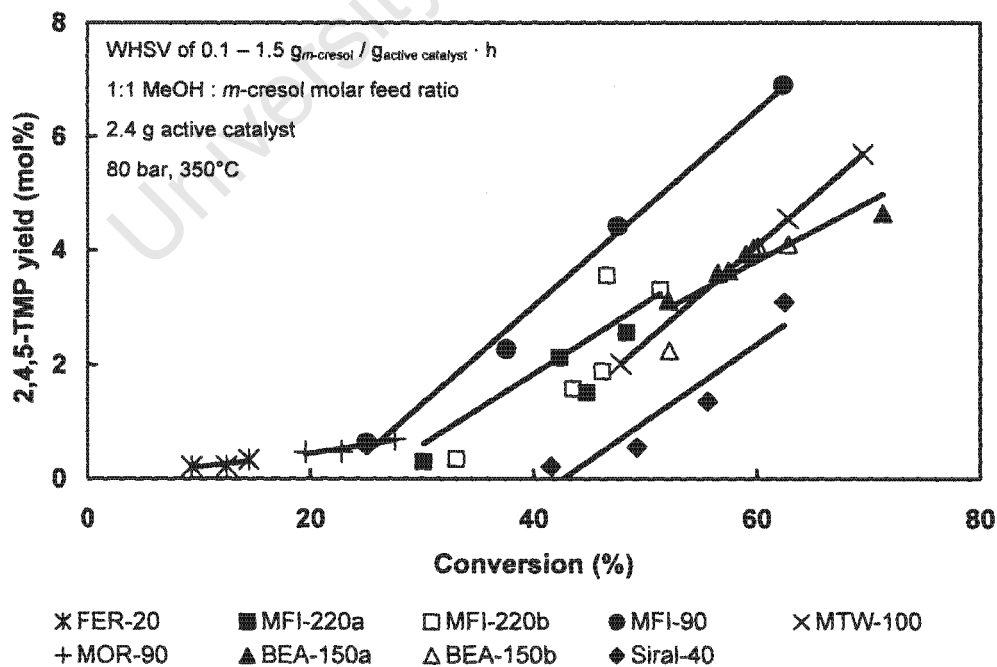


Figure 5-41: 2,4,5-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.5 Selectivity to and yield of 2,4,6-trimethylphenol

Figures 5-42 and 5-43 show the selectivity to and yield, respectively, of 2,4,6-trimethylphenol achieved over the catalysts tested.

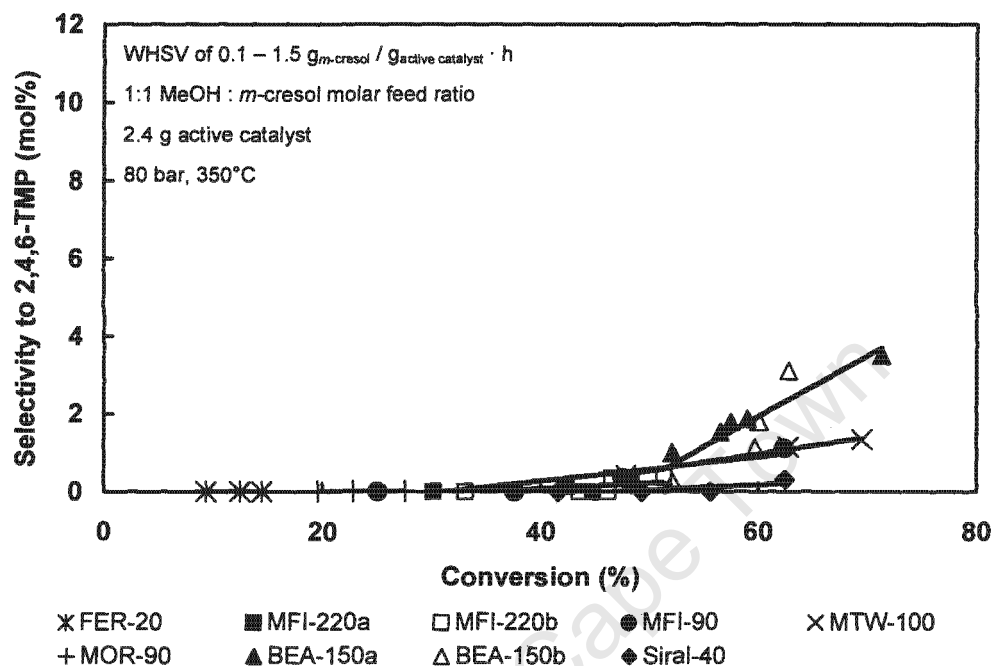


Figure 5-42: Selectivity to 2,4,6-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

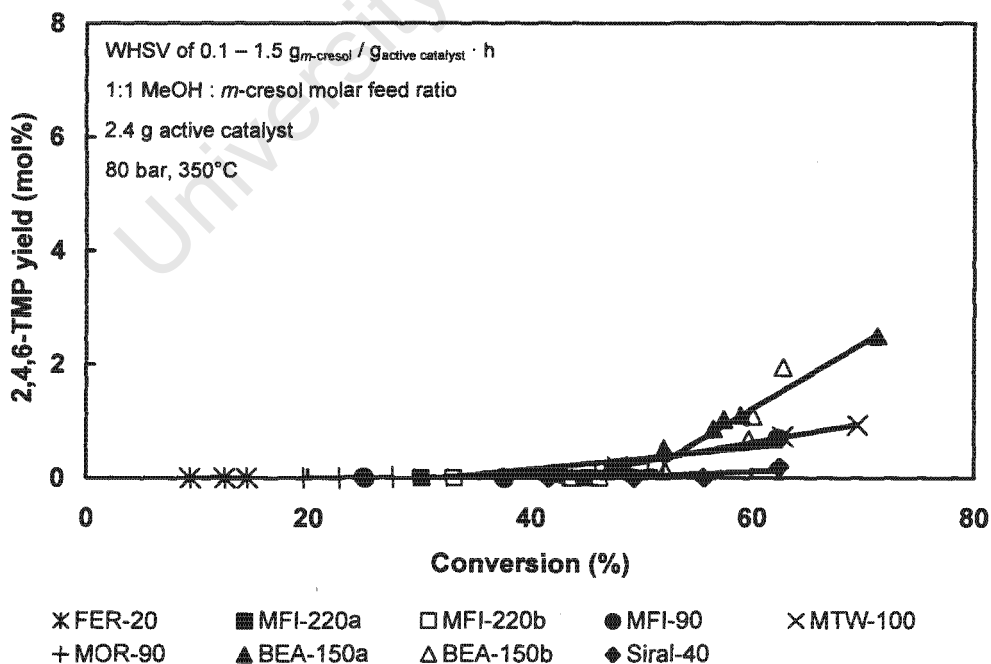


Figure 5-43: 2,4,6-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.6 Selectivity to and yield of 3,4,5-trimethylphenol

Figures 5-44 and 5-45 show the selectivity to and yield, respectively, of 3,4,5-trimethylphenol achieved over the catalysts tested.

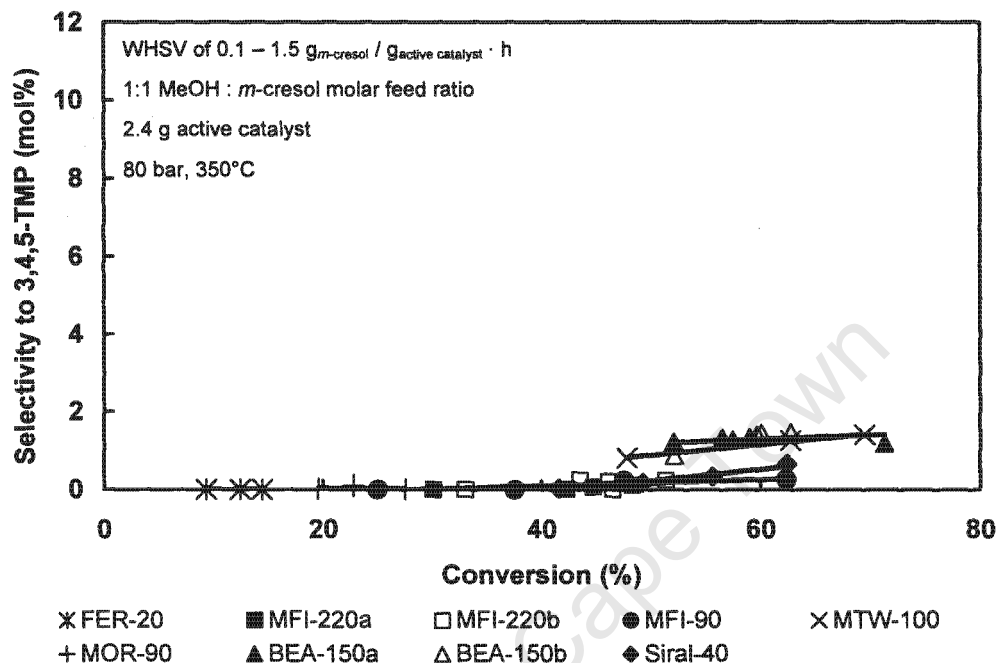


Figure 5-44: Selectivity to 3,4,5-trimethylphenol versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

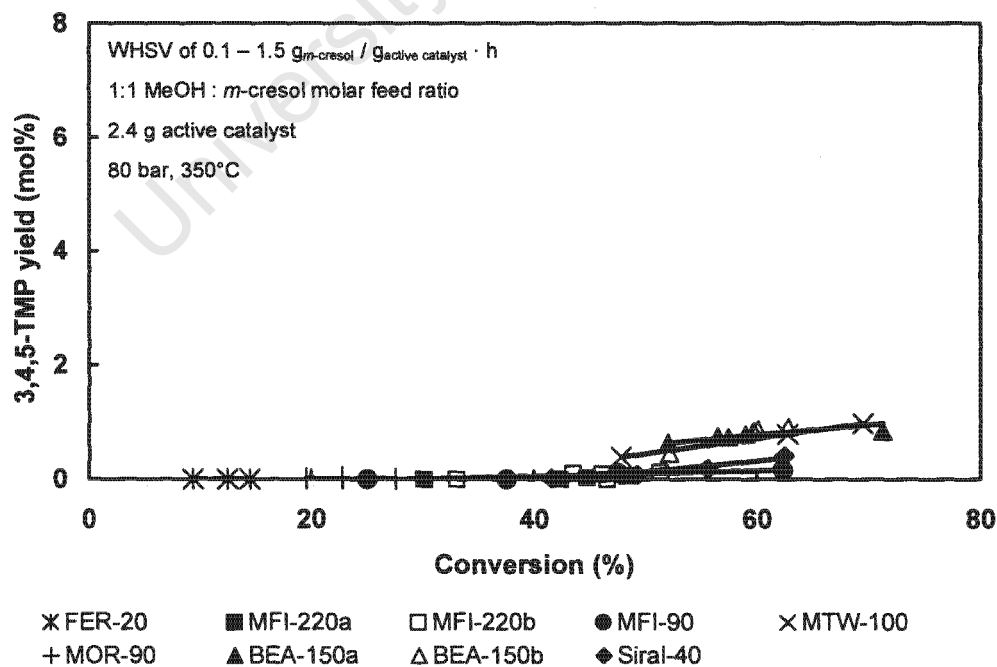


Figure 5-45: 3,4,5-Trimethylphenol yield versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

5.3.7.7 Summary of trimethylphenols selectivities and yields

As stated in the introduction to section 5.3.7, both selectivities and yields of trimethylphenols are constantly increasing, the higher the *m*-cresol conversion, the higher these values. Table 5-5 summaries the results obtained for the distributions of trimethylphenols over catalysts tested. While the total trimethylphenol selectivities and yields are comparable over all catalysts tested, total trimethylphenol product is lowest over Siral-40 (see figure 5-31). In general 2,4,5-trimethylphenol is most abundant over the zeolites while 2,3,6-trimethylphenol is most abundant over Siral-40.

Over medium pore zeolites MFI-90 and, somewhat less pronounced, over MFI-220, 2,4,5-trimethylphenol is much predominating. Selectivity to and yield of all individual isomers is low over Siral-40, corresponding to the low selectivity and yield of total trimethylphenols.

Table 5-5: Distribution of the trimethylphenol isomers (mol %) over catalysts tested (for base case reaction conditions, see table 5-1). Some of the data ranges have been extrapolated slightly using the trend lines.

a. For conversion of 15 – 20 % (trimethylphenol distributions in mol %)

	Catalyst						
	FER-20	MFI-90	MFI-220	MOR-90	MTW-100	BEA-150	Siral-40
2,3,4-TMP	10			8			
2,3,5-TMP	2			18			
2,3,6-TMP	42			33			
2,4,5-TMP	46			39			
2,4,6-TMP	0			0			
3,4,5-TMP	0			1			

b. For conversion of 40 % (trimethylphenol distributions in mol %)

	Catalyst						
	FER-20	MFI-90	MFI-220	MOR-90	MTW-100	BEA-150	Siral-40
2,3,4-TMP		2	0				2
2,3,5-TMP		3	8				6
2,3,6-TMP		28	44				58
2,4,5-TMP		66	46				31
2,4,6-TMP		2	1				0
3,4,5-TMP		1	1				3

c. For conversion of 50 % (trimethylphenol distributions in mol %)

	Catalyst						
	FER-20	MFI-90	MFI-220	MOR-90	MTW-100	BEA-150	Siral-40
2,3,4-TMP		2	1		11	15	6
2,3,5-TMP		4	9		15	16	9
2,3,6-TMP		26	30		32	27	51
2,4,5-TMP		64	57		32	32	31
2,4,6-TMP		3	2		4	3	0
3,4,5-TMP		1	2		6	7	4

d. For conversion of 60 % (trimethylphenol distributions in mol %)

	Catalyst						
	FER-20	MFI-90	MFI-220	MOR-90	MTW-100	BEA-150	Siral-40
2,3,4-TMP		2			11	17	9
2,3,5-TMP		5			17	20	11
2,3,6-TMP		24			30	22	43
2,4,5-TMP		63			32	28	31
2,4,6-TMP		5			4	8	1
3,4,5-TMP		2			6	6	4

It was not possible to accurately extrapolate data for all the catalysts over the full range of conversion. So it has not been possible to compare the distribution of trimethylphenol isomers at similar levels of conversion for all the catalysts.

Over FER-20, for low conversion of 15 %, no 2,4,6-TMP or 3,4,5-TMP were formed and only a relatively small amount of 2,3,5-TMP was formed. There was some 2,3,4-TMP, but the majority of the trimethylphenol product comprised 2,3,6-TMP and 2,4,5-TMP, which were formed at a similar prevalence (42 and 46 % respectively).

Over MOR-90, at low conversion of 20 %, practically none of the isomers 2,4,6-TMP or 3,4,5-TMP were formed. The most abundant isomer was 2,4,5-TMP (39 %) followed by 2,3,6-TMP (33 %). A reasonable amount of 2,3,5-TMP was formed (18 %) and a smaller amount of 2,3,4-TMP (8 %).

For conversion of 40 % it is possible to compare trimethylphenol isomer distribution between the two MFI zeolites and Siral-40. Over MFI-90 the most prominent isomer was 2,4,5-TMP (66 %) followed by 2,3,6-TMP (28 %). Over MFI-220 similar proportions of

2,4,5- and 2,3,6-TMP were formed (46 and 44 % respectively). In comparison, over Siral-40, 2,3,6-TMP was the most abundant TMP (58 %), followed by 2,4,5-TMP (31 %). Comparatively small amounts of the other TMP isomers were produced over these catalysts.

For conversion of 50 % MFI-90, MFI-220, MTW-100, BEA-150 and Siral-40 can be compared. MFI-90 and MFI-220 produced highest proportions of 2,4,5-TMP (64 and 57 % respectively). The TMP distributions over MTW-100 and BEA-150 were very similar. In contrast to the zeolites, Siral-40 again produced more 2,3,6-TMP than 2,4,5-TMP (51 and 31 % respectively). This trend was unique to Siral-40.

For conversion of 60 % MFI-90, MTW-100, BEA-150 and Siral-40 can be compared. MFI-90 produced the highest proportion of 2,3,4-TMP (63 %). The distributions of 2,3,6-TMP and 2,4,5-TMP over MTW-100 and BEA-150 were similar. Siral-40 produced proportionally more 2,3,6-TMP than 2,4,5-TMP (43 and 31 % respectively).

5.3.8 "Others"

"Others" included all ring compounds, excluding cresols, xylenols, 3-methylanisole and trimethylphenols. So, "others" could include phenol, diphenylethers, dimethylanisoles and tetramethylphenols. Producing "others" is a disadvantage as it is unlikely these compounds will have much use.

Selectivity to "others" was, in general, relatively constant, though increasing slightly with conversion and ranging between 8.5 mol % and 26.3 mol %, over the range of conversion achieved (figure 5-46). In comparison amongst the catalysts tested, the increase in selectivity over MFI-220 and Siral-40 was steepest.

At higher levels of conversion (71 %) up to 17 mol % "others" yield was seen over BEA-150 and MTW-100 (figure 5-47). Correspondingly Siral-40 and MFI-220 showed the steepest increase in yield of "others" with increasing conversion.

Over all catalysts it was noticed that within the phenolic product the proportion of "others" remained quite constant again at between conversions of 21 % and 30 % thus suggesting that conversion does not have much effect in that regard (figure 5-48). However, note that "others" contains compounds that are not regarded as "phenolic product" in the narrow sense (such as diphenylethers or higher methylated anisoles). The consumption of the latter (higher methylated anisoles) with increasing conversion may have balanced the enhanced formation of the higher phenolics.

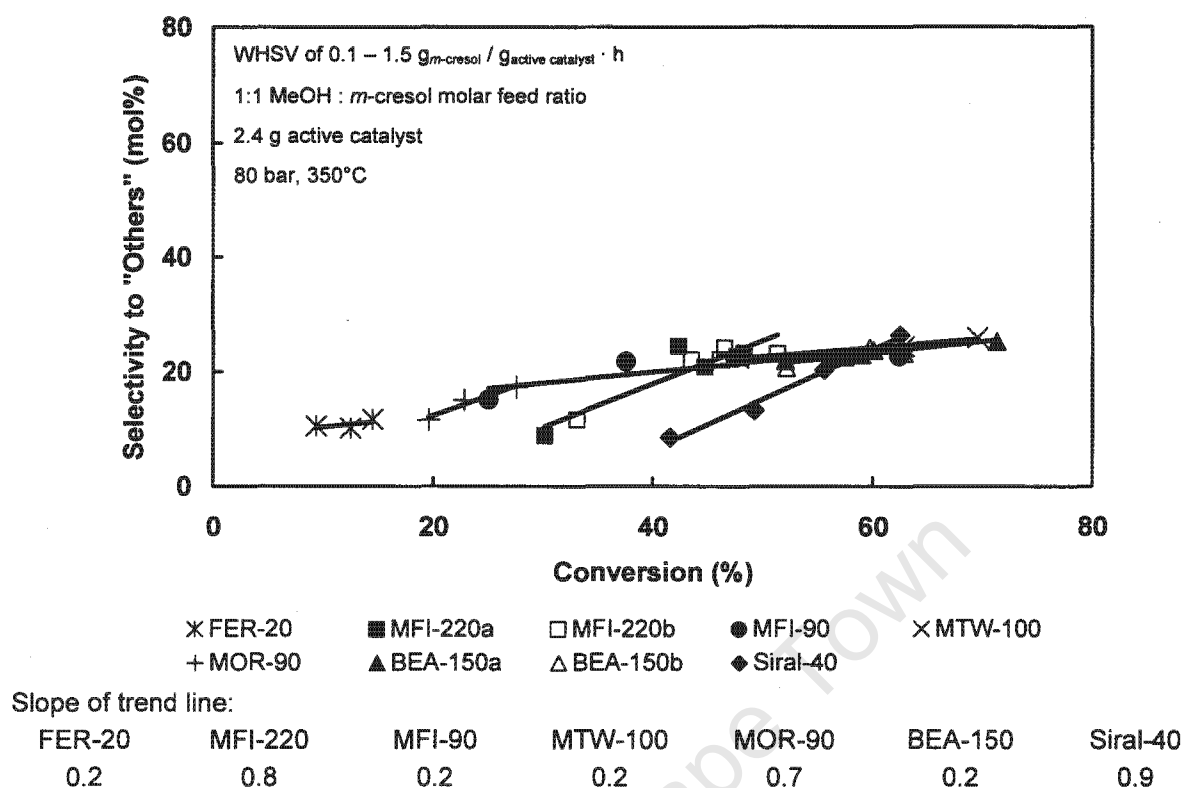


Figure 5-46: Selectivity to "others" versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

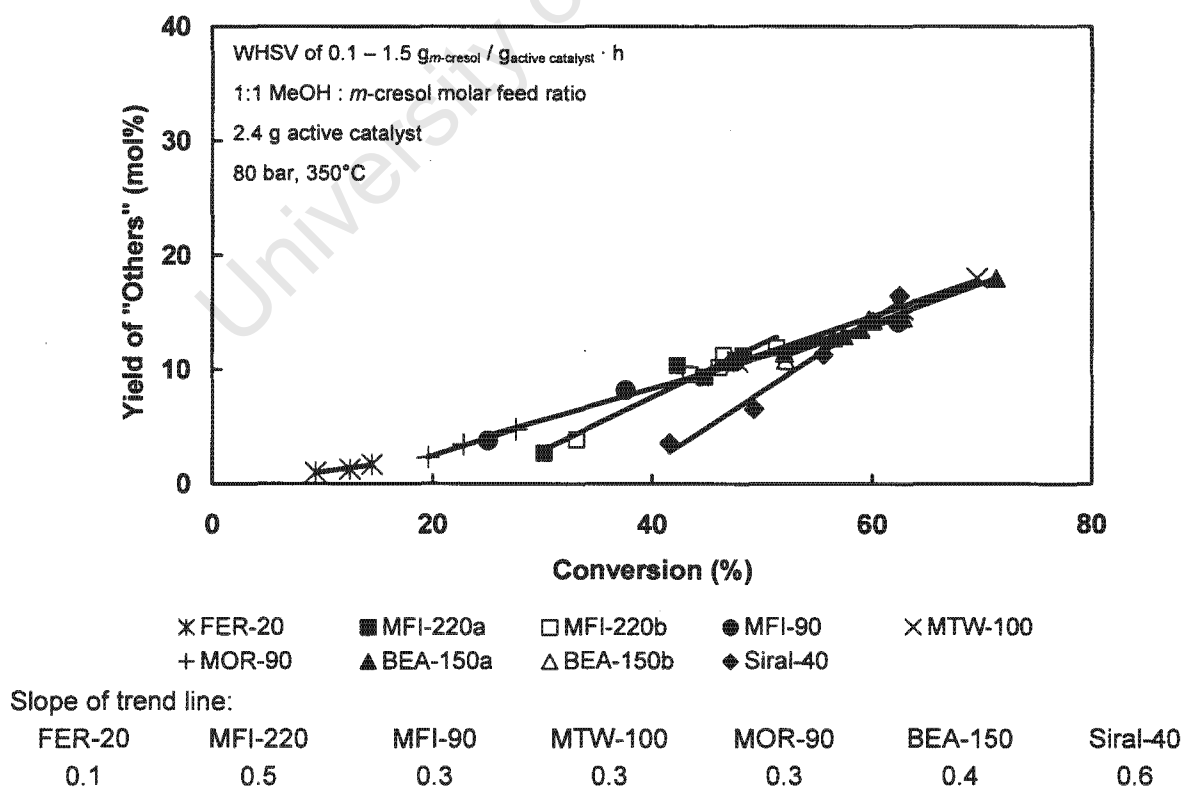


Figure 5-47: Yield of "others" versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested

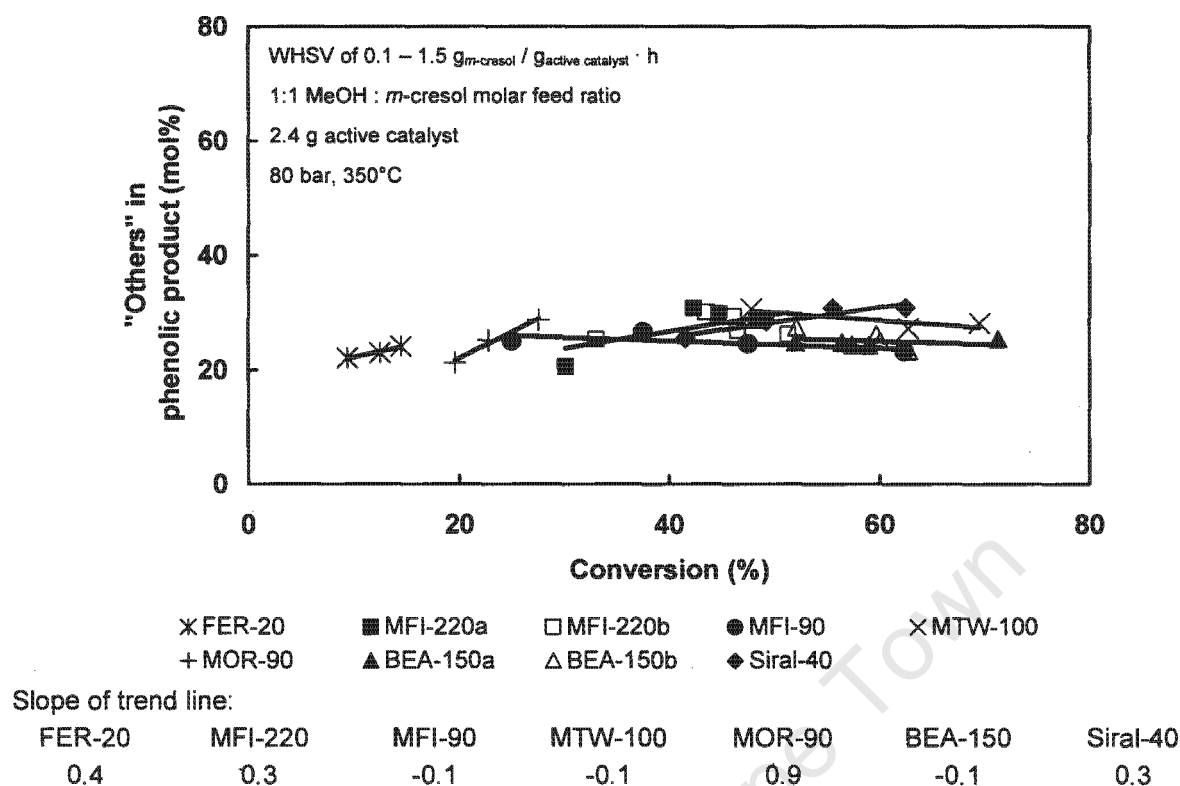


Figure 5-48: Distribution to "others" within phenolic product versus *m*-cresol conversion for *m*-cresol methylation over catalysts tested. Note that "others" does not only consist of phenolic compounds.

5.3.9 Presence of *o*- and *p*-cresol

Product analyses indicated the presence of some *o*- and *p*-cresol (see figure 5-49). The amount seen in product analyses was higher than what was seen when the raw feed was tested for impurities, thus indicating that some isomerisation took place. Generally less than 2 mol % was yielded but two data points showed a maximum yield of 7 mol % over MFI-90 and 3.5 mol % over BEA-150 while Siral-40 produced, comparably the lowest amounts. However, the aforementioned data point obtained from MFI-90 might still be an outlier (figure 5-37). Over most catalysts the proportion of cresol isomers increased with conversion but over MOR-90 data scatter masked this most probable trend.

5.4 Xylenol isomers distribution

This section compares the distribution of xylene isomers within xylene product over catalysts tested for the alkylation of *m*-cresol with methanol. The results were obtained at the reaction conditions shown in the figures.

5.4.1 Xylenol isomers distribution over all catalysts tested

Figure 5-50 shows the combined distribution of xylene isomers within the total xylene product over all catalysts tested under the conditions stated. It can be seen that the proportion of 2,5-xylene within the xylene product was highest but decreased over the entire range of conversion. In comparison, the distribution of 3,4- and 2,3-xylene is flat through the range, while the percentages of 2,4-, 3,5-, and 2,6-xylene increase as conversion increases. However, the increase of the latter is on a low level. The scatter of data points for 3,4- and 2,3-xylene are particularly high.

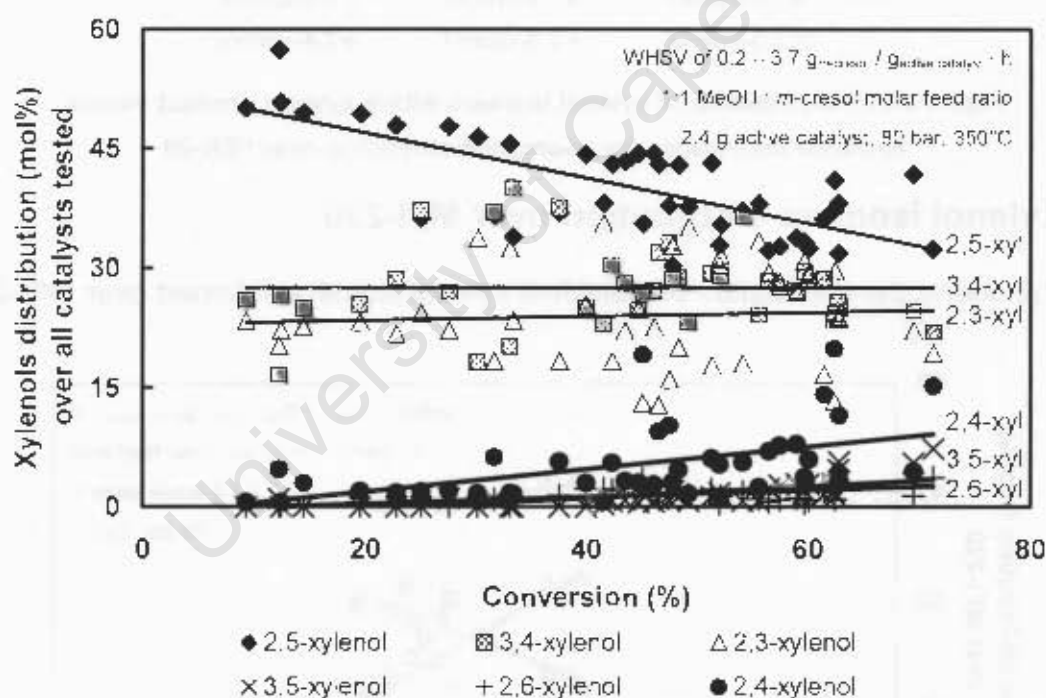


Figure 5-50: Distribution of xylene isomers within xylene product versus *m*-cresol conversion from *m*-cresol methylation over all the catalysts tested

Note that even at the highest conversion of 71 %, xylene isomer distribution is still far from equilibrium (see figure 5-10). The following sections, 5.4.2 to 5.4.8, show the xylene distributions over the individual catalysts. Trends and levels are generally the same as in figure 5-50, however, due to the small number of data points for each catalyst, individual trend lines are less robust and generally negatively influenced by data scatter.

5.4.2 Xylenol isomers distribution over FER-20

Figure 5-51 shows the distribution of individual xylenol isomers obtained over FER-20.

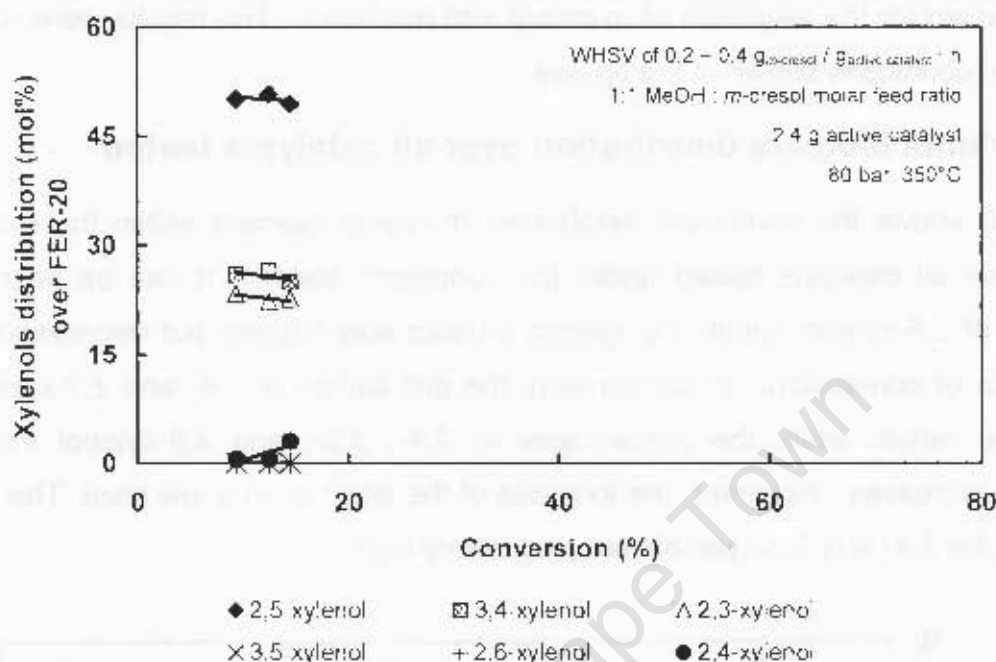


Figure 5-51: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over FER-20

5.4.3 Xylenol isomers distribution over MFI-220

Figure 5-52 shows the distribution of individual xylenol isomers obtained over MFI-220.

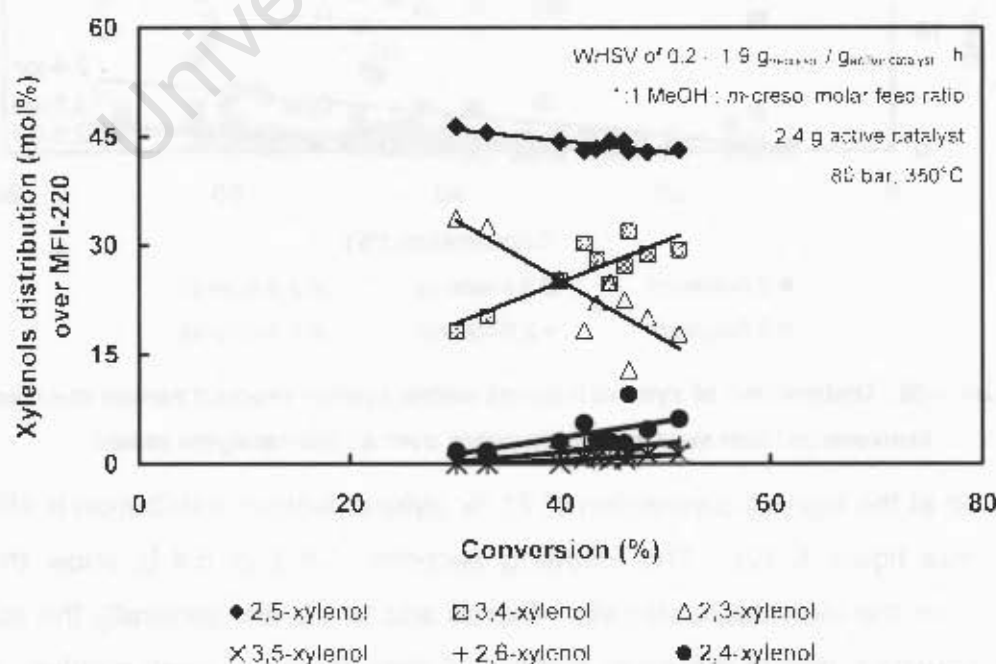


Figure 5-52: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over MFI-220

5.4.4 Xylenol isomers distribution over MFI-90

Figure 5-53 shows the distribution of individual xylene isomers obtained over MFI-90.

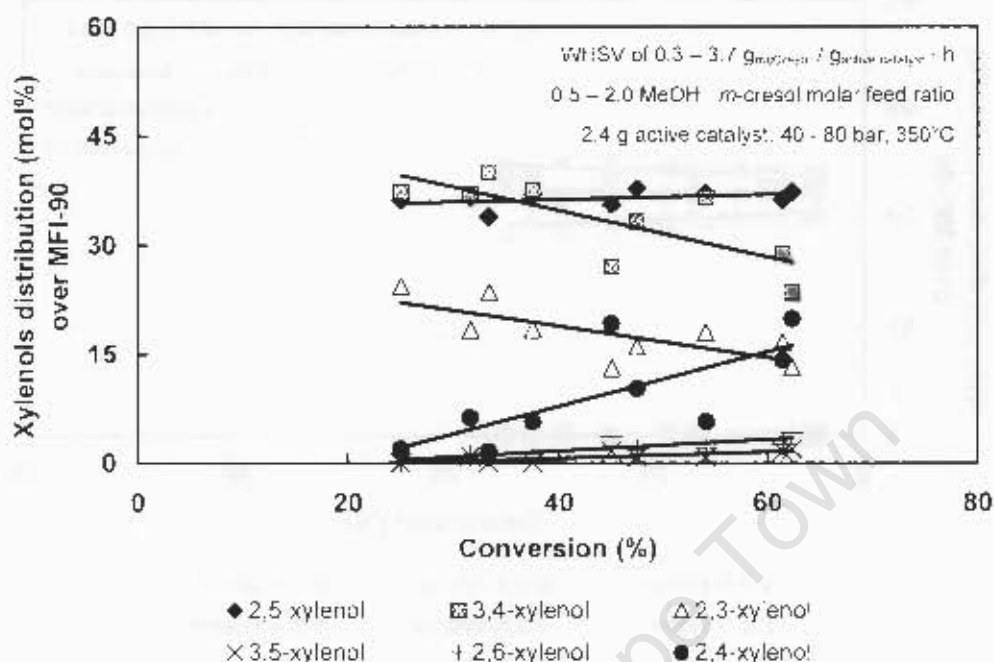


Figure 5-53: Distribution of xylene isomers within xylene product versus $m\text{-cresol}$ conversion for $m\text{-cresol}$ methylation over MFI-90 at reaction pressure of 40 bar and 80 bar

Figure 5-54a shows the distribution of individual xylene isomers obtained over 9.6 g of MFI-90 and correspondingly very low WHSV of 0.05 - 1.5 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$.

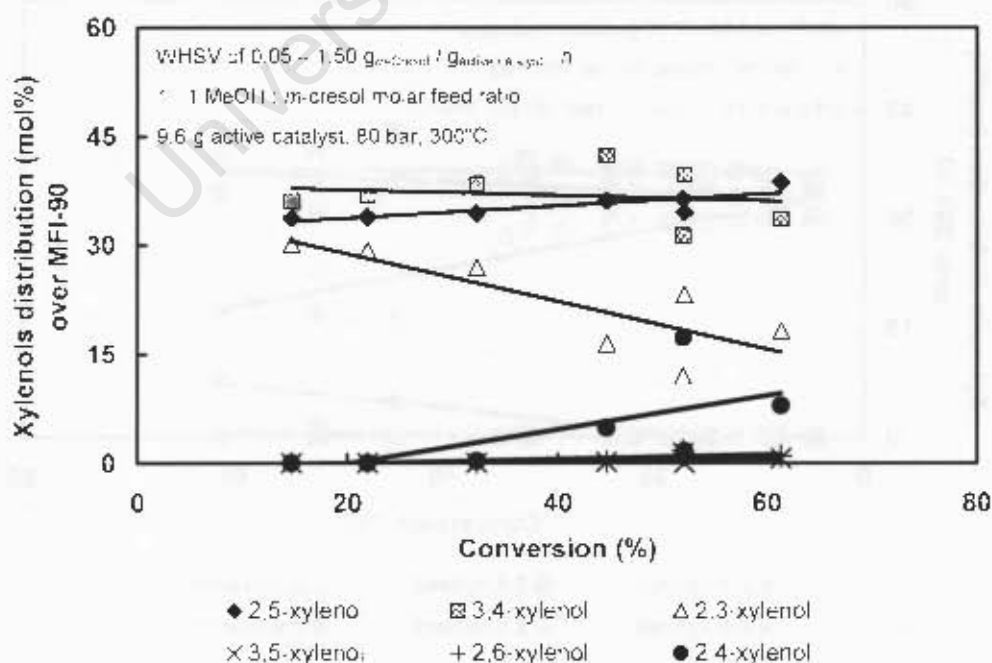


Figure 5-54a: Distribution of xylene isomers within xylene product versus $m\text{-cresol}$ conversion for $m\text{-cresol}$ methylation over MFI-90 at a reaction temperature of 300°C (9.6 g of zeolite)

Figure 5-54b shows the distribution of individual xylenol isomers obtained over 2.4 g of MFI-90 and correspondingly very low WHSV of 0.2 – 2.6 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$.

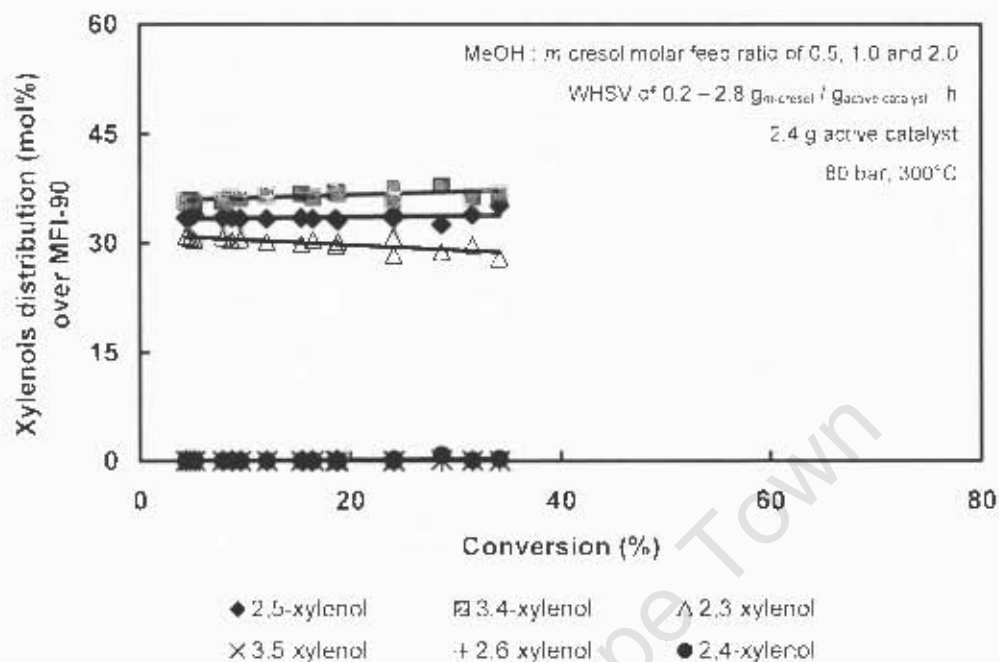


Figure 5-54b: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over MFI-90 at a reaction temperature of 300°C (2.4 g of zeolite)

Figure 5-55 shows the distribution of individual xylenol isomers obtained over 2.4 g and 9.6 g of MFI 90 (this figure combines the results shown in figures 5-42a and b).

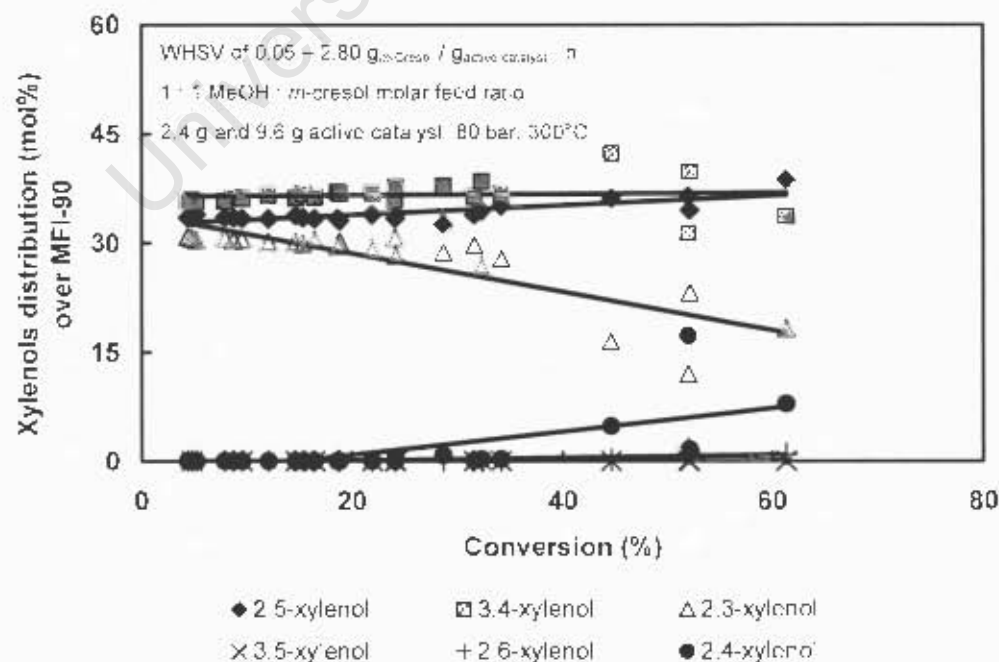


Figure 5-55: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over MFI-90 at a reaction temperature of 300°C (combination of results achieved over 2.4 g of zeolite and 9.6 g of zeolite)

5.4.5 Xylenol isomers distribution over MTW-100

Figure 5-56 shows the distribution of individual xylenol isomers obtained over MTW-100.

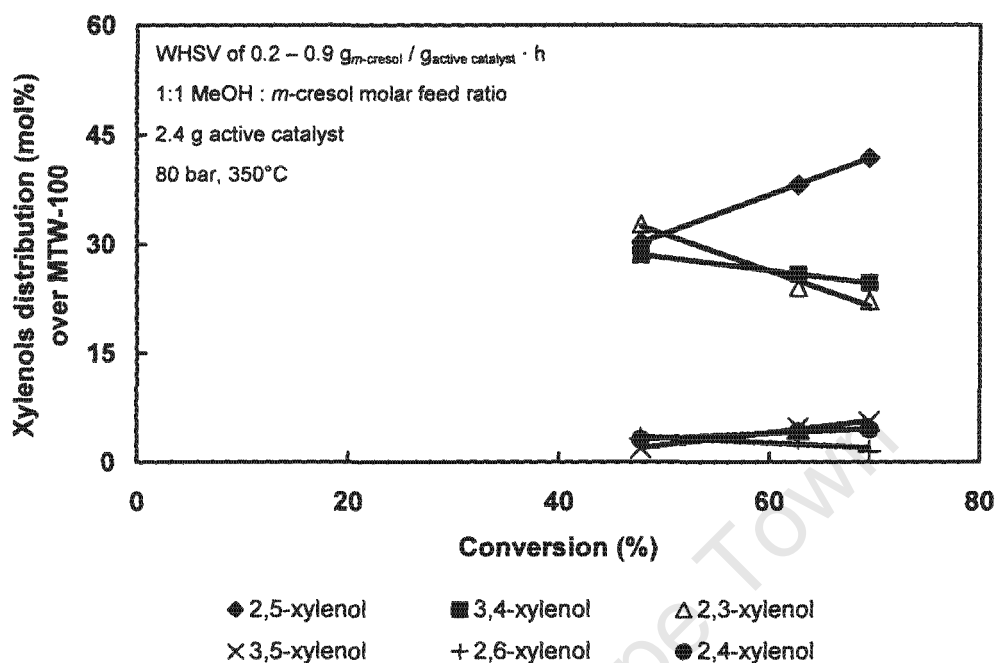


Figure 5-56: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over MTW-100

5.4.6 Xylenol isomers distribution over MOR-90

Figure 5-57 shows the distribution of individual xylenol isomers obtained over MOR-90.

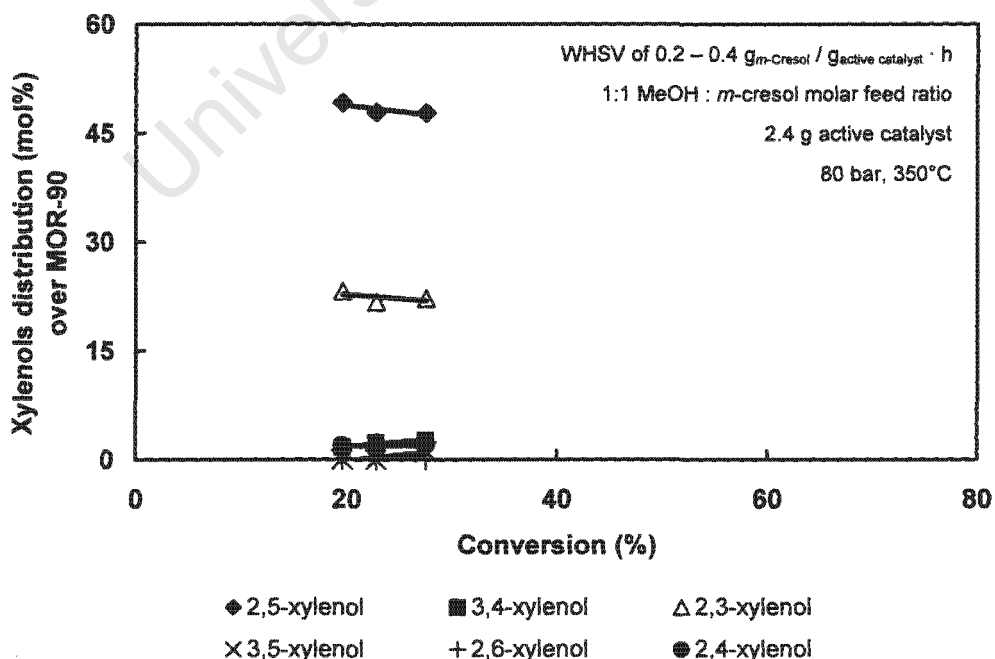


Figure 5-57: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over MOR-90

5.4.7 Xylenol isomers distribution over BEA-150

Figure 5-58 shows the distribution of individual xylenol isomers obtained over BEA-150.

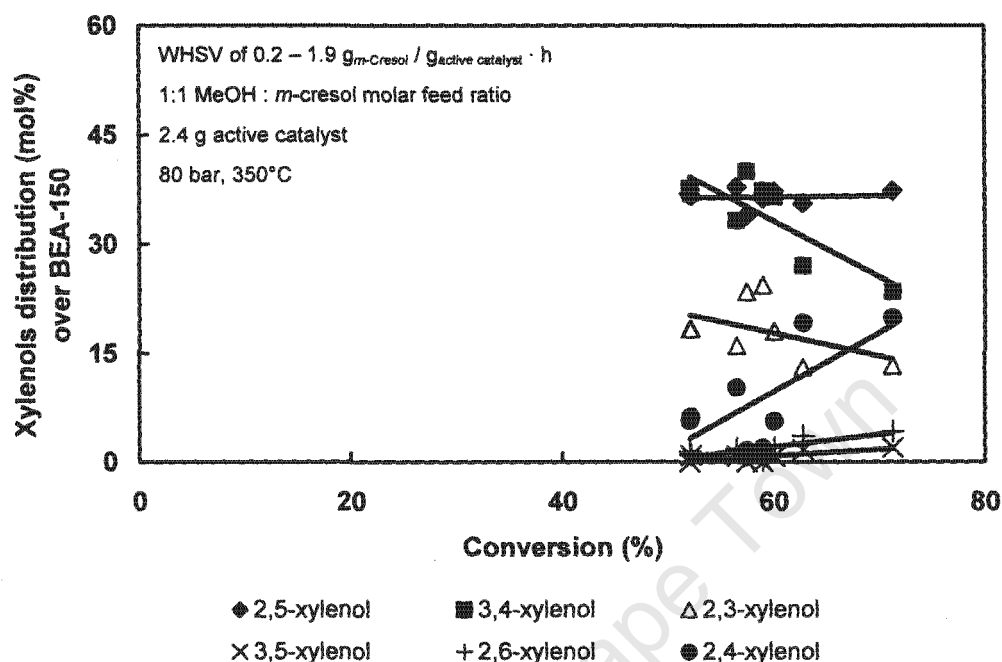


Figure 5-58: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over BEA-150

5.4.8 Xylenol isomers distribution over Siral-40

Figure 5-59 shows the distribution of individual xylenol isomers obtained over Siral-40.

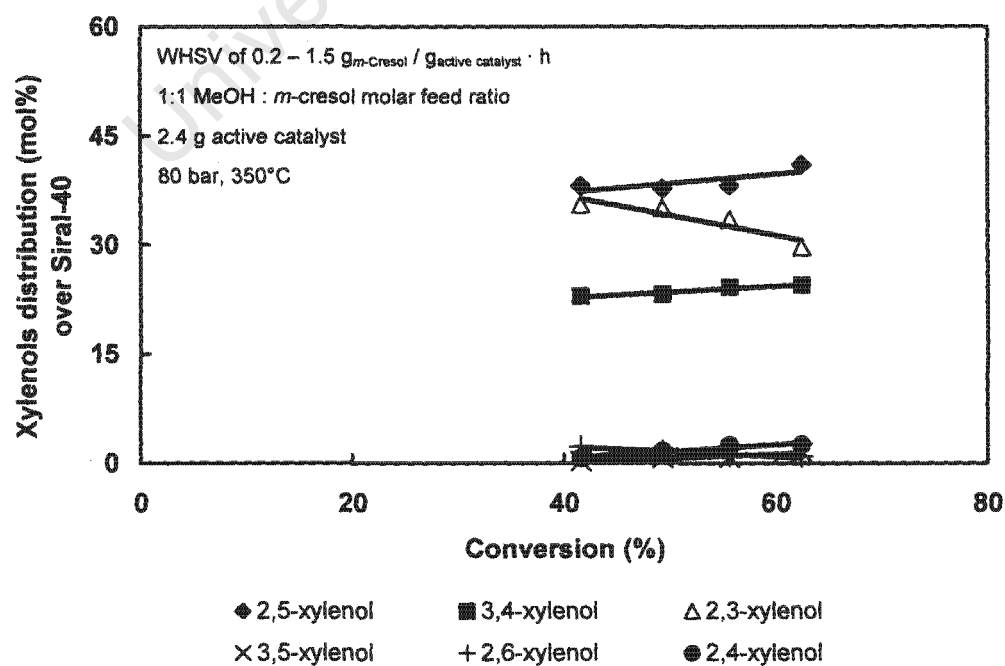


Figure 5-59: Distribution of xylenol isomers within xylenol product versus *m*-cresol conversion for *m*-cresol methylation over Siral-40

5.5 Effect of reaction conditions

The effect of variation in reaction conditions was investigated over MFI-90. Parameter settings (temperature, pressure, methanol : *m*-cresol molar feed ratio and WHSV) were varied around the base case conditions (for base case conditions, see table 5-1). These results are presented in the following sections (raw data is tabulated in appendix 3).

5.5.1 Reaction temperature effect

The reactions were carried out at two different temperatures, 300 and 350°C, over 2,4 g active MFI-90, at pressure of 80 bar. Three sets of data points were produced varying methanol : *m*-cresol molar feed ratios (and due to limited adjustability of pump settings, of $\text{WHSV}_{m\text{-cresol}}$ simultaneously, see appendix 6). Ratio of methanol : *m*-cresol and $\text{WHSV}_{m\text{-cresol}}$ combinations applied were 0.5 / 0.25, 1.0 / 0.37 and 2.0 / 0.43 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$ (see section 4.4.7). Collecting data from only two different temperature settings appears insufficient for trend establishment, however for each temperature settings, several data points were collected for different space velocity / feed ratio combinations (see figure 5-60), so that trends could be confirmed as far as possible.

5.5.1.1 *m*-Cresol conversion at different reaction temperatures and calculation of corresponding activation energy

Figure 5-60 shows conversion achieved at 300°C and 350°C over MFI-90.

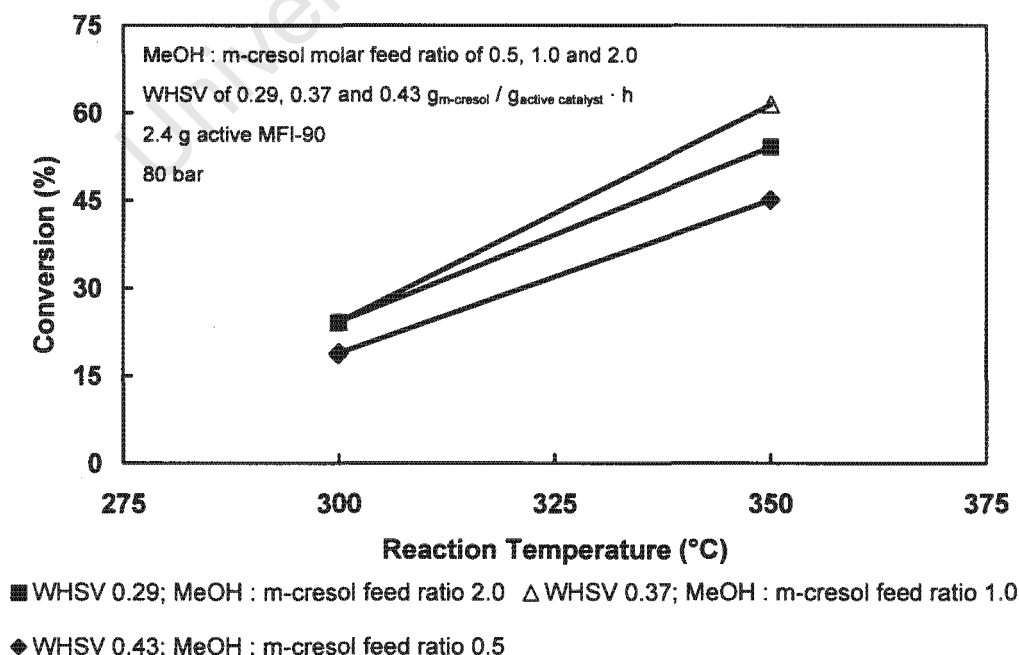


Figure 5-60: Conversion of *m*-cresol for *m*-cresol methylation over MFI-90 at different reaction temperatures

Conversion increased steeply from between 19 and 24 % at 300°C to between 45 and 61 % at 350°C (figure 5-60). Apparent activation energies, for the overall reaction of *m*-cresol methylation with methanol to total products, calculated from these three lines averaged 86 kJ / mol (table 5-6 and appendix 5). Activation energies to the primary products have also been calculated.

Table 5-6: Activation energies to different products for reactions in which temperature was varied (see appendix 5 for detailed calculations). Activation energies have been calculated for the first order reaction (see sections 5.5.5 and 6.4.4.1 and appendix 5).

Reaction	Activation Energy (E_A) (kJ / mol)
<i>m</i> -Cresol + methanol, overall conversion of <i>m</i> -cresol	86
<i>m</i> -Cresol + methanol → 2,5-xylenol + water	72
<i>m</i> -Cresol + methanol → 3,4-xylenol + water	54
<i>m</i> -Cresol + methanol → 2,3-xylenol + water	25
<i>m</i> -Cresol + methanol → sum of major xylenol isomers + water	59

5.5.1.2 Selectivity to total xylenols at different reaction temperatures

Figure 5-61 shows selectivity to total xylenol product at 300°C and 350°C over MFI-90. The selectivity to total xylenol isomers increased only a little from between 38 and 41 mol % to between 42 and 52 mol %, respectively.

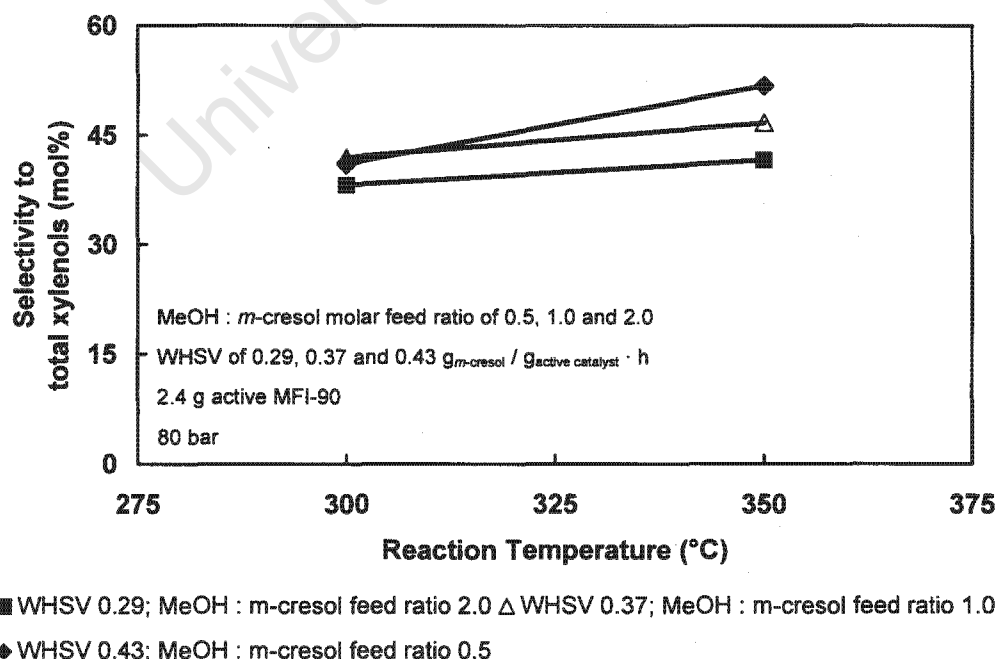


Figure 5-61: Selectivity to total xylenols for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.3 Total xylenols yield at different reaction temperatures

Figure 5-62 shows total xynolol yield at 300°C and 350°C over MFI-90. The yield of total xynolol isomers increased steeply with reaction temperature as well.

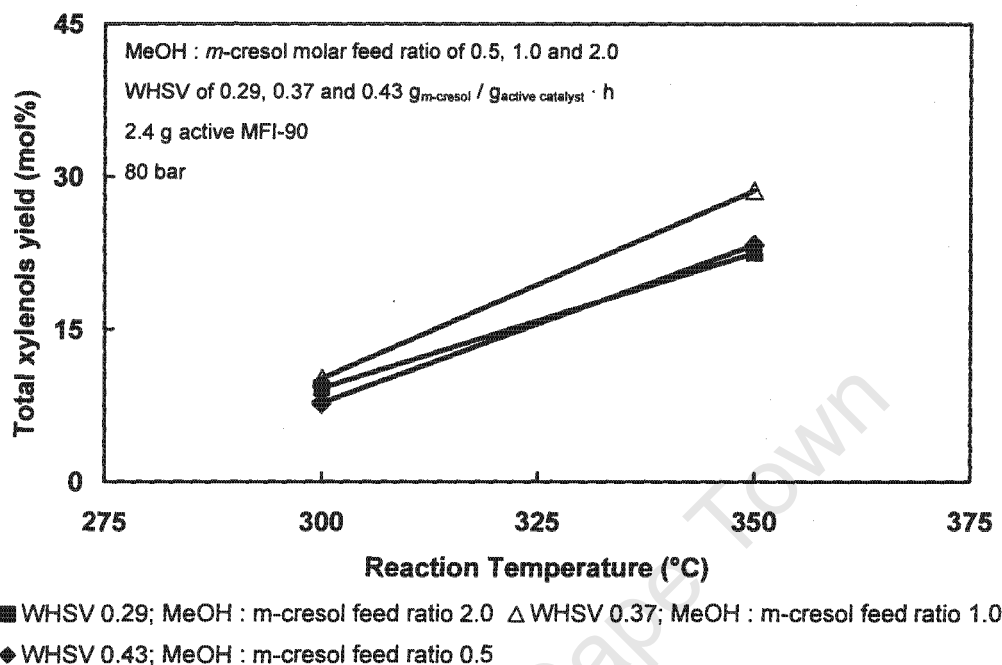


Figure 5-62: Total xylenols yield for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.4 Total xylenols within phenolic product at different reaction temperatures

Figure 5-63 shows total xylenols in phenolic product at 300°C and 350°C over MFI-90. The proportion of total xylenols in the phenolic product showed a moderate decline from between 66 and 74 mol % (at 300°C) to between 46 and 53 mol % (at 350°C) as shown in figure 5-63. Note that these selectivity variations are affected by both change in temperature and conversion.

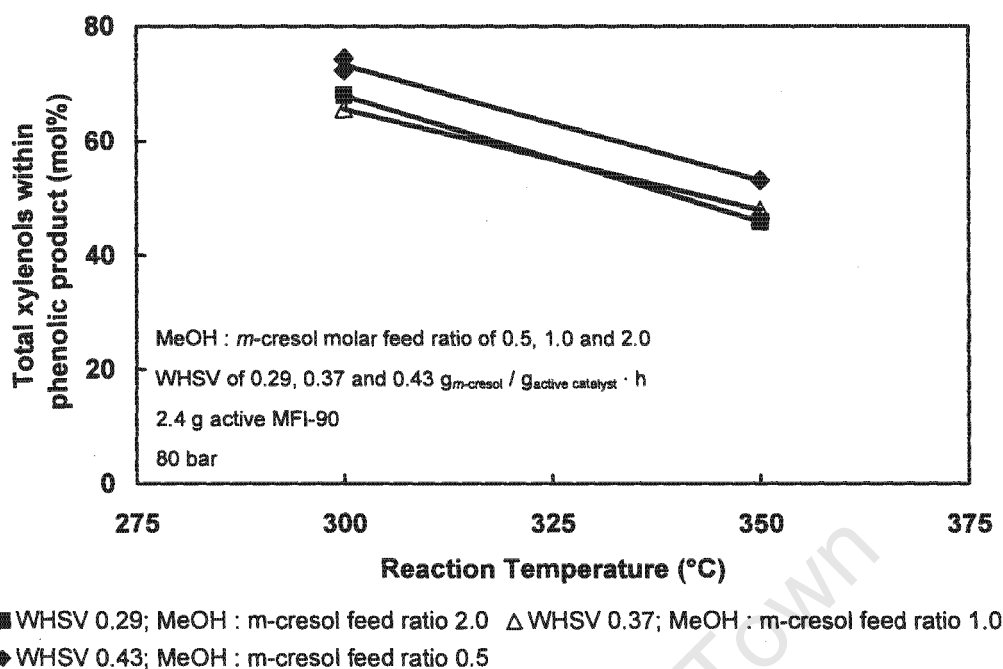


Figure 5-63: Proportion of total xylenols within phenolic product for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.5 Selectivity to 3-methylanisole at different reaction temperatures

Figure 5-64 shows selectivity to 3-methylanisole at 300°C and 350°C over MFI-90. Selectivity to 3-methylanisole showed a steep decline, falling from between 36 and 45 mol % (at 300°C) to between 3 and 10 mol % (at 350°C).

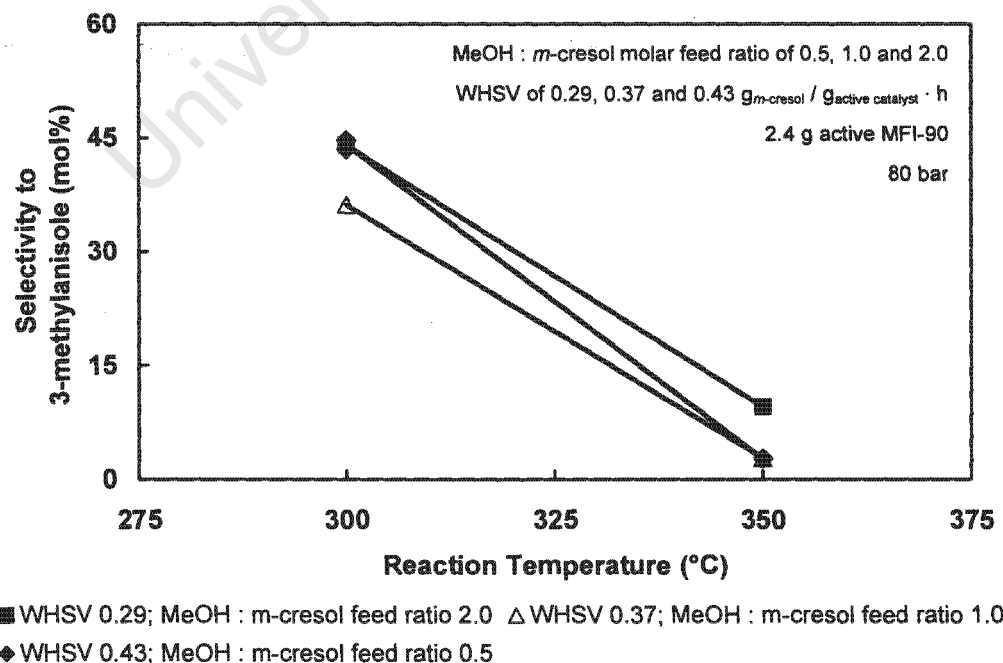


Figure 5-64: Selectivity to 3-methylanisole for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.6 Selectivity to trimethylphenols at different reaction temperatures

Figure 5-65 shows selectivity to trimethylphenols at 300°C and 350°C over MFI-90. Selectivity to TMPs showed a significant increase with increasing reaction temperature.

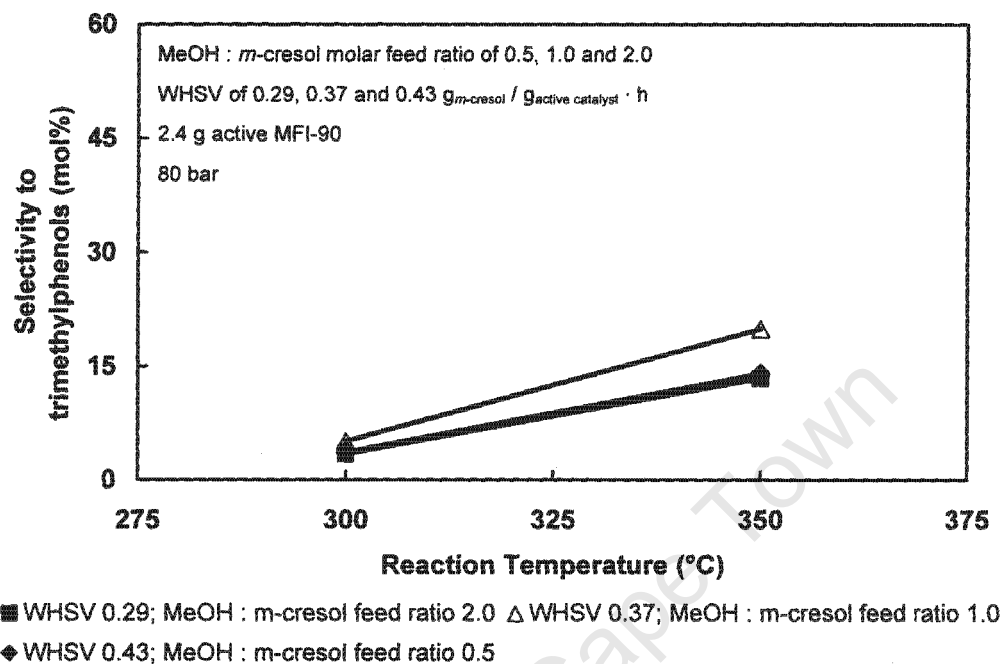


Figure 5-65: Selectivity to trimethylphenols for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.7 Selectivity to "others" at different reaction temperatures

Figure 5-66 shows selectivity to "others" at 300°C and 350°C over MFI-90. Selectivity to "others" showed a significant increase with increasing reaction temperature.

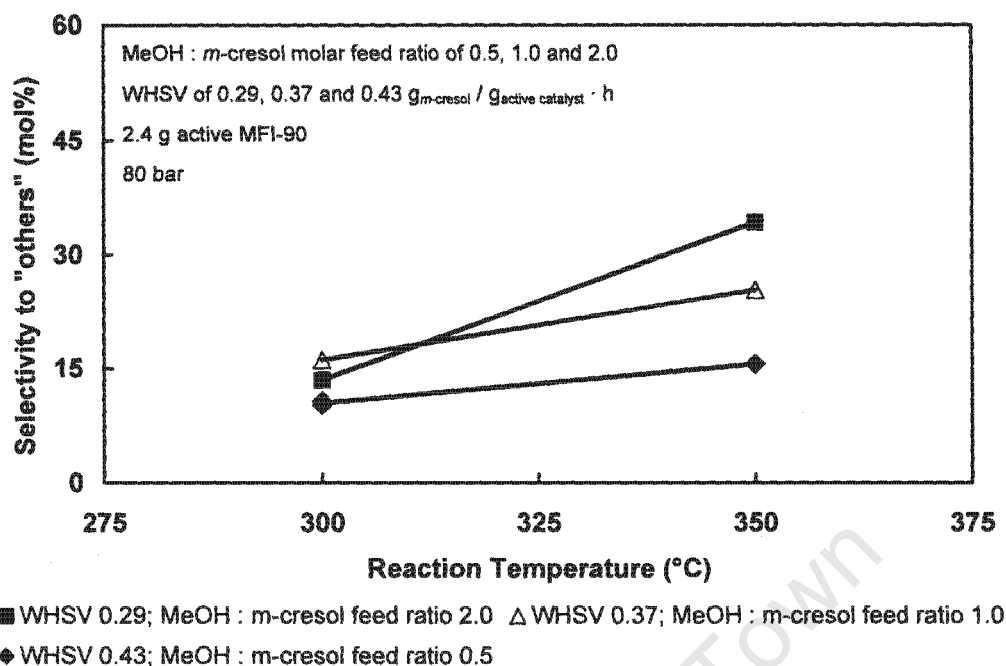


Figure 5-66: Selectivity to "others" for *m*-cresol methylation over MFI-90 at different reaction temperatures

5.5.1.8 Selectivity to individual xylenol isomers at different reaction temperatures

Figure 5-67 shows selectivity to 2,5-xylenol at 300°C and 350°C over MFI-90. Selectivity to 2,5-xylenol increased from ca. 14 mol % to ca. 17 mol %.

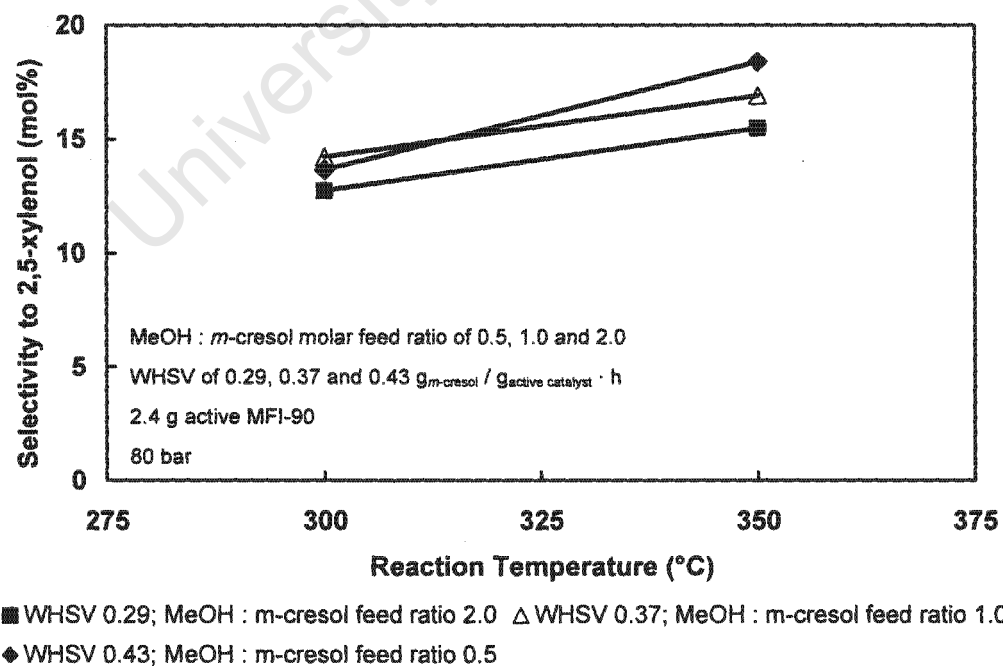


Figure 5-67: Selectivity to 2,5-xylenol for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-68 shows selectivity to 3,4-xylenol at 300°C and 350°C over MFI-90. The selectivity to 3,4-xylenol remained relatively constant at reaction temperatures of 300°C and 350°C.

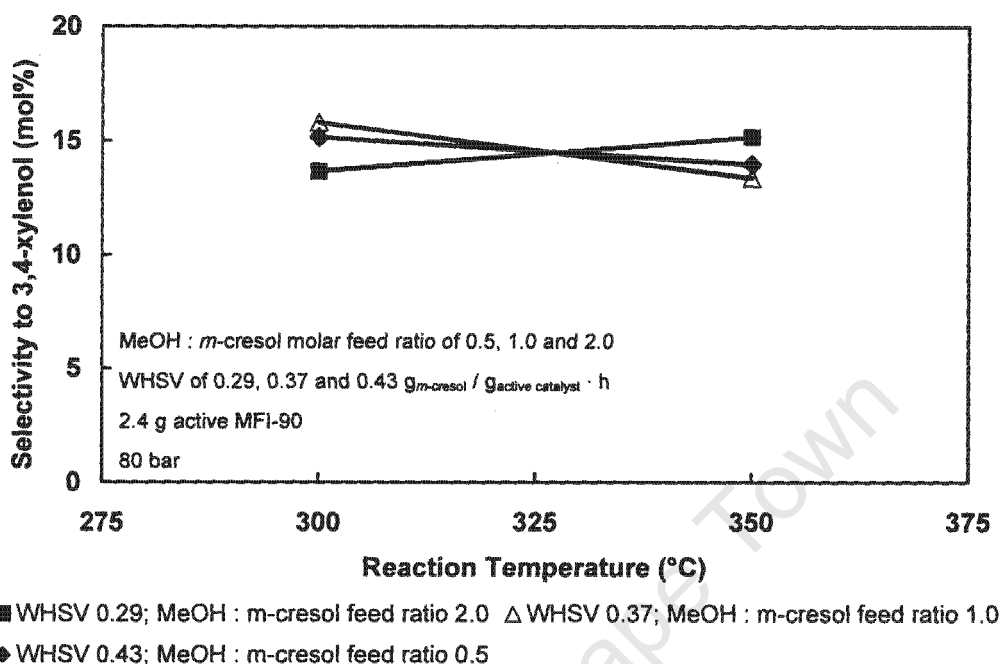


Figure 5-68: Selectivity to 3,4-xylenol for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-69 shows selectivity to 2,3-xylenol at 300°C and 350°C over MFI-90. Selectivity to 2,3-xylenol showed a decrease as reaction temperature was increased from 300°C to 350°C.

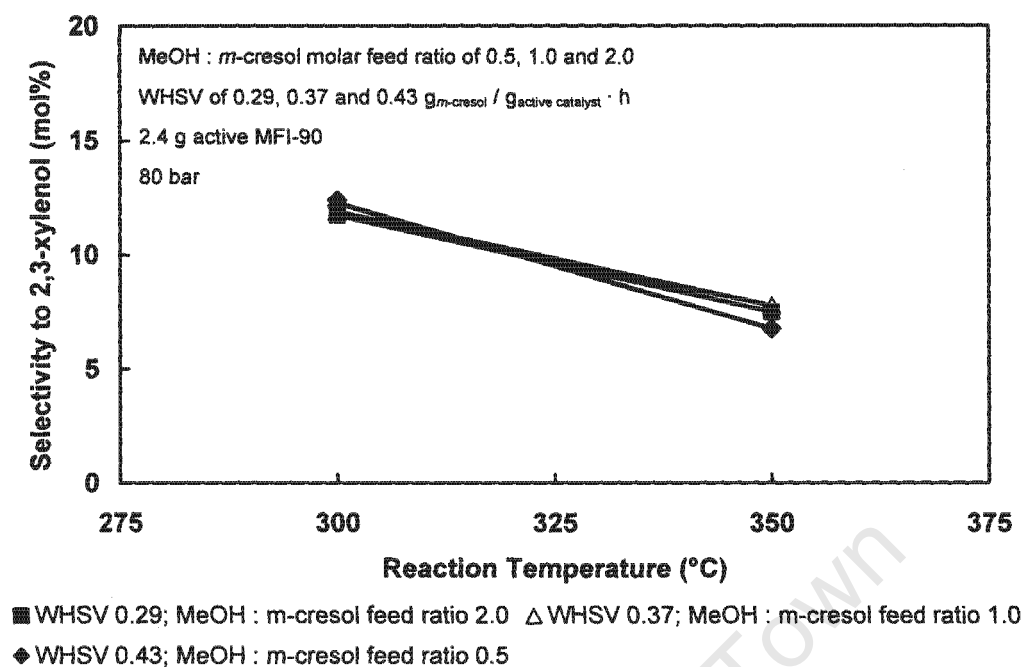


Figure 5-69: Selectivity to 2,3-xylene for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-70 shows selectivity to 3,5-xylene at 300°C and 350°C over MFI-90. Practically no 3,5-xylene was produced at 300°C, but at 350°C small amounts (selectivity < 1 mol %) were present.

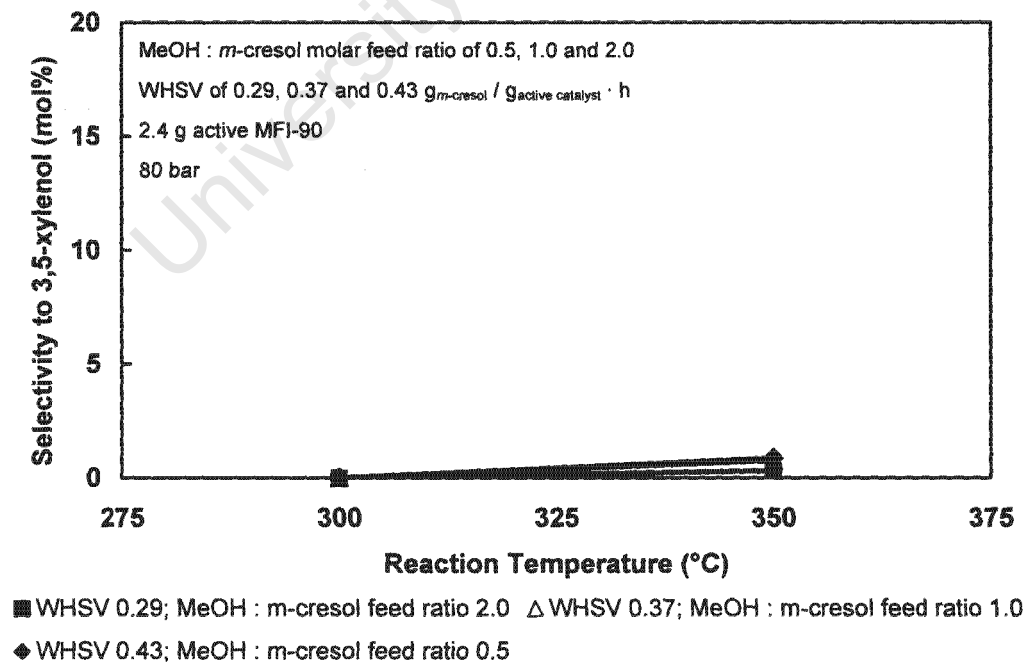


Figure 5-70: Selectivity to 3,5-xylene for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-71 shows selectivity to 2,6-xylenol at 300°C and 350°C over MFI-90. Practically no 2,6-xylenol was produced at 300°C, but at 350°C selectivities to 2,6-xylenol were between 1 and 2 mol %.

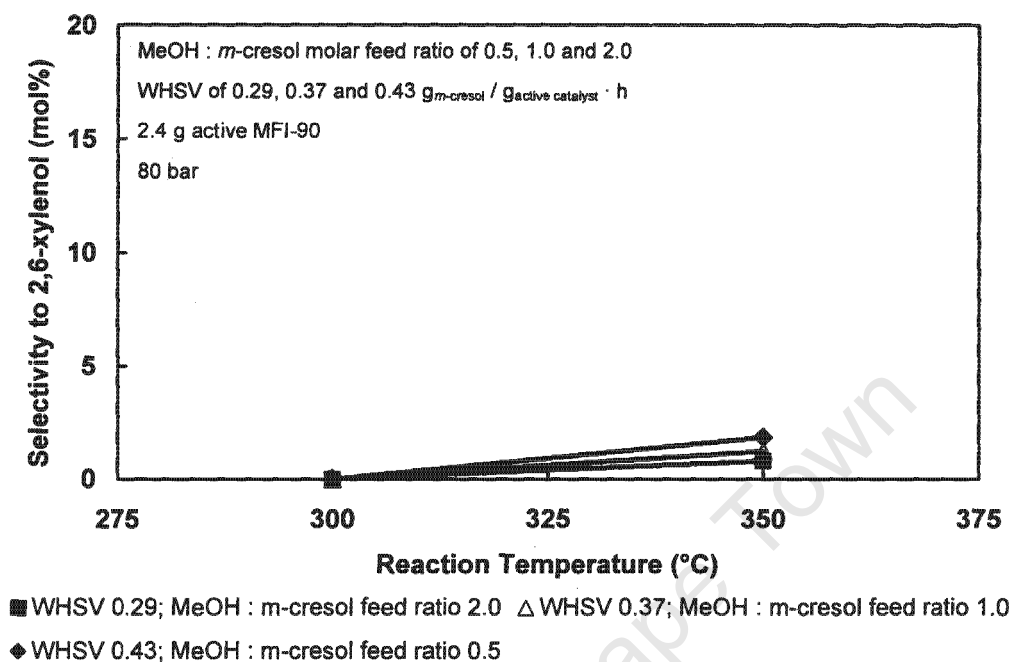


Figure 5-71: Selectivity to 2,6-xylenol for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-72 shows selectivity to 2,4-xylenol at 300°C and 350°C over MFI-90. Selectivity to 2,4-xylenol was practically zero at 300°C, but increased to between 2 and 10 mol % at 350°C.

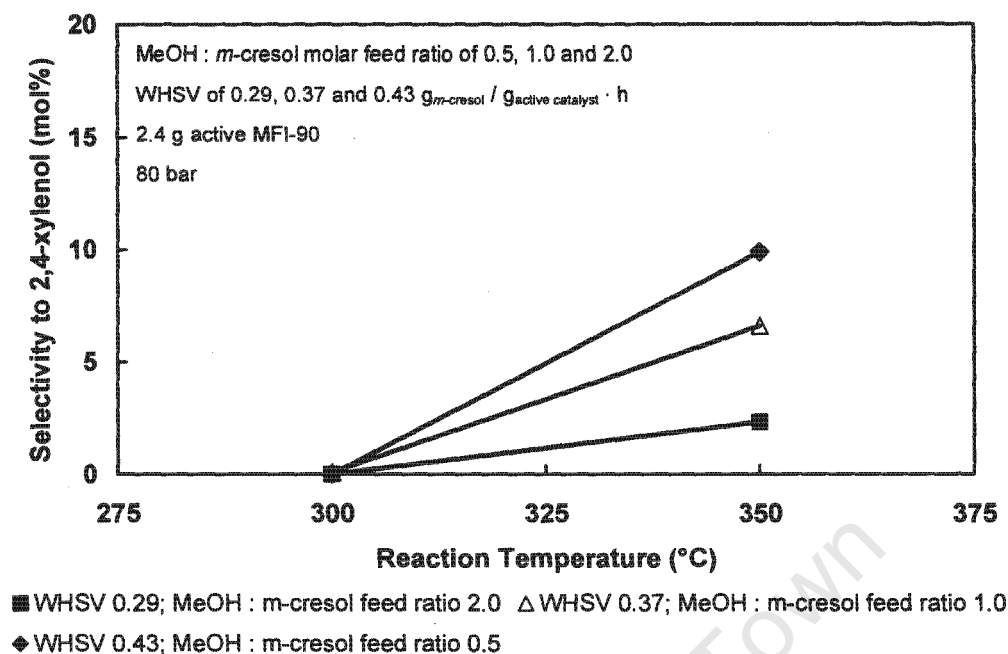


Figure 5-72: Selectivity to 2,4-xylene for *m*-cresol methylation over MFI-90 at different reaction temperatures

Figure 5-73 shows distribution of xylene isomers produced in methylation of *m*-cresol with methanol at 300°C and 350°C over MFI-90. For comparison the calculated ideal gas equilibrium distributions are also shown (see appendix 1, thermodynamic data from Daubert *et al.*, 1999). It be seen that only isomers 2,5-, 3,4- and 2,3-xylene were present at 300°C. At 350°C, distribution included some 2,4-xylene and small amounts of 3,5- and 2,6-xylene, largely at the expense of 2,3-xylene.

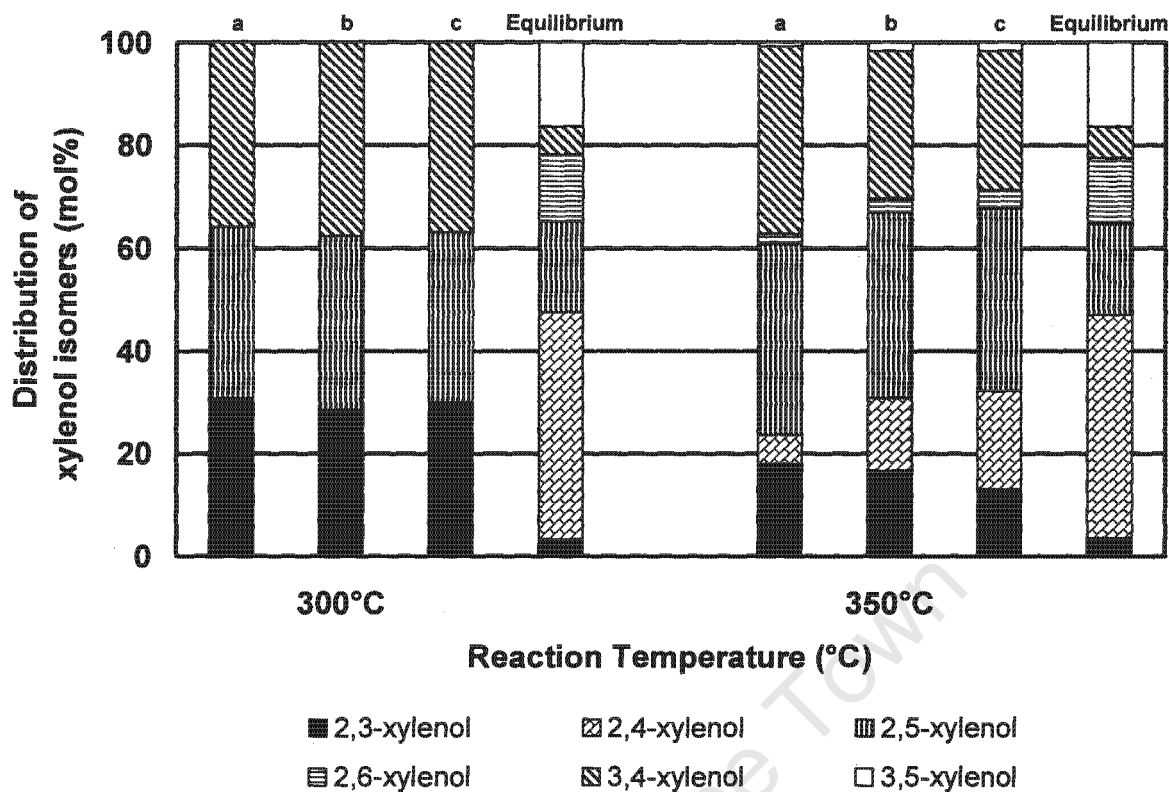


Figure 5-73: Selectivity to xyleneol isomers for methylation of *m*-cresol over 2.4 g MFI-90 at two different reaction temperatures, 300°C and 350°C at 80 bar. Data shown pertain to:

- a:** WHSV of 0.29 g_{*m*-cresol} / g_{active catalyst} · h and MeOH : *m*-cresol molar feed ratio of 2.0, with conversion of 24 % at 300°C and 54 % at 350°C
- b:** WHSV of 0.37 g_{*m*-cresol} / g_{active catalyst} · h and MeOH : *m*-cresol molar feed ratio of 1.0 with conversion of 24 % at 300°C and 61 % at 350°C
- c:** WHSV of 0.43 g_{*m*-cresol} / g_{active catalyst} · h and MeOH : *m*-cresol molar feed ratio of 0.5 with conversion of 19 % at 300°C and 45 % at 350°C

Equilibrium: Calculated ideal gas phase thermodynamic equilibrium at 300°C and 350°C (see appendix 1, thermodynamic data from Daubert *et al.*, 1999).

For experiments conducted at 350°C, samples were collected after ~ 360 hours-on-stream (a), after ~180 hours-on-stream (b) and after ~250 hours-on-stream (c). It is likely that catalyst deactivation and data scatter affected both measured conversion and product distribution.

5.5.2 Reaction pressure effect

As discussed in previous sections (see sections 2.10.2, 4.3.3 and 4.3.6), the reactions were conducted at elevated pressures in attempt to keep the phenolic portion of the feed in liquid phase thus ensuring the catalysts were kept wet and the reaction took place in liquid phase as far as possible. The aim of this was to limit coking by washing high molecular coke precursors away from the catalysts.

A brief investigation into the effect of pressure on the methylation reaction was carried out. Although groups of data from only two different settings were collected, which is insufficient for reliable trend establishment, the data are represented here.

Methylation of *m*-cresol was carried out over MFI-90 at 30 and 80 bar (constant temperature of 300°C and WHSV of 0.1 g_{*m*-cresol} / g_{active catalyst} · h) and also at 40 and 80 bar (constant temperature of 350°C and WHSV of 3.7 g_{*m*-cresol} / g_{active catalyst} · h).

5.5.2.1 *m*-Cresol conversion at different reaction pressures

Figure 5-74 shows conversion of *m*-cresol at 40 and 80 bar over MFI-90.

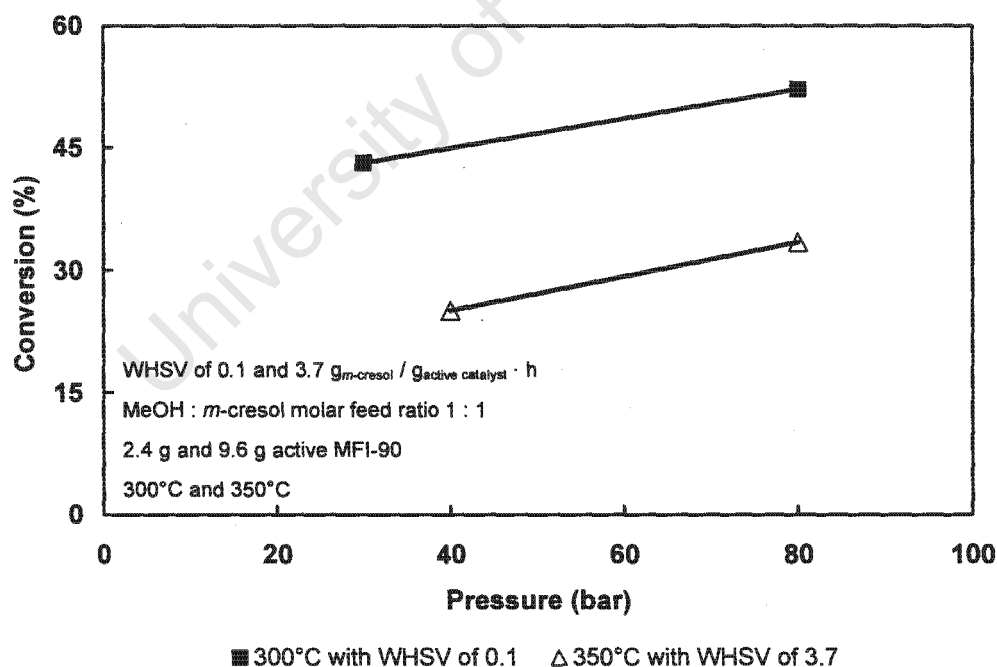


Figure 5-74: Conversion of *m*-cresol versus reaction pressure for *m*-cresol methylation over MFI-90

Conversion of *m*-cresol increased with increasing pressure, however, only moderately (figure 5-74).

5.5.2.2 Selectivity to total xylenols at different reaction pressures

Figure 5-75 shows selectivity to total xynol isomers at 40 and 80 bar over MFI-90. The selectivity to total xylenols increased for increasing reaction pressure, however, moderately. The selectivities were very similar for different reaction temperature, space velocity and conversion.

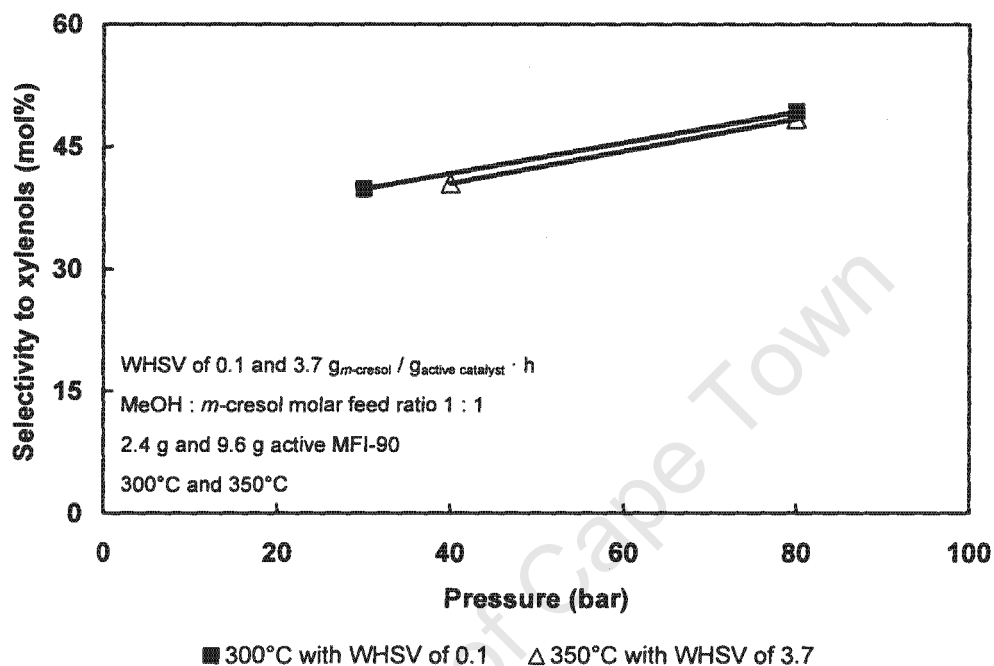


Figure 5-75: Selectivity to total xylenols versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.3 Total xylenols yield at different reaction pressures

Figure 5-76 shows total xynol isomers yield at 40 and 80 bar over MFI-90. Total xynol isomers yield increased at a rate steeper than that for conversion and selectivity, being the product of the two (figure 5-76).

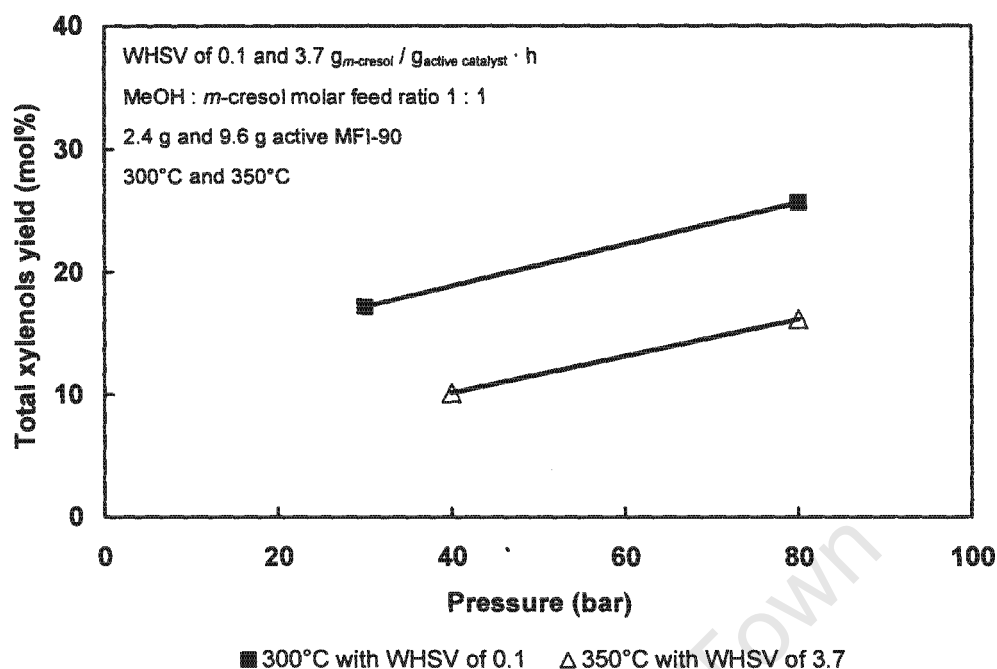


Figure 5-76: Total xylenols yield versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.4 Total xylenols within phenolic product at different reaction pressures

Figure 5-77 shows proportion of total xylenols at 40 and 80 bar over MFI-90. The proportion of total xylenols within the phenolic product remained almost constant for the conditions tested (figure 5-77).

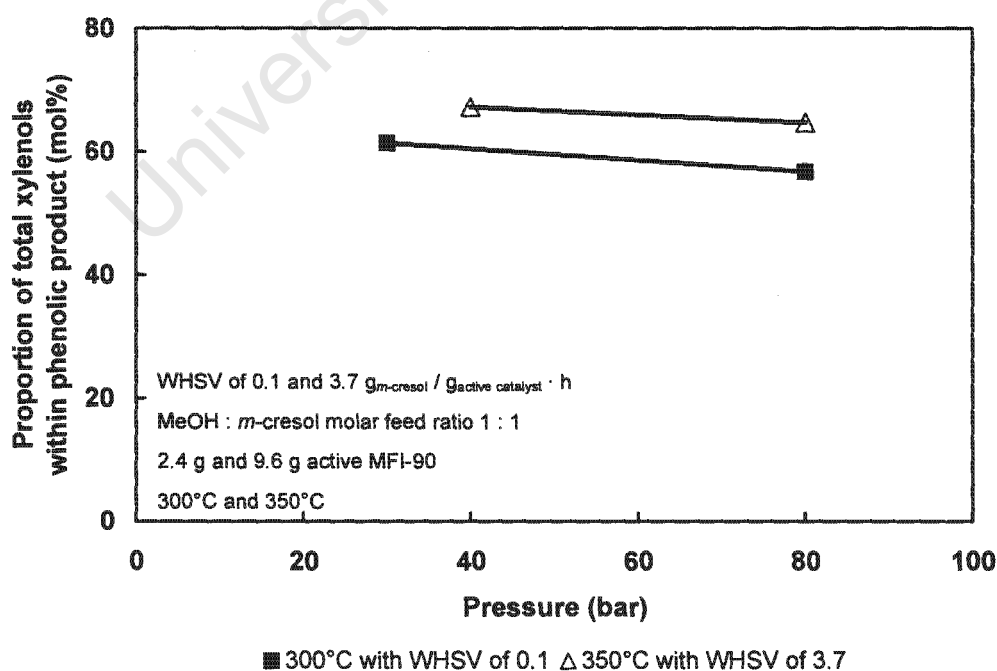


Figure 5-77: Proportion of total xylenols within phenolic product versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.5 Selectivity to 3-methylanisole at different reaction pressures

Figure 5-78 shows selectivity to 3-methylanisole at 40 and 80 bar over MFI-90. Selectivity to 3-methylanisole decreased significantly for increasing reaction pressure (figure 5-78).

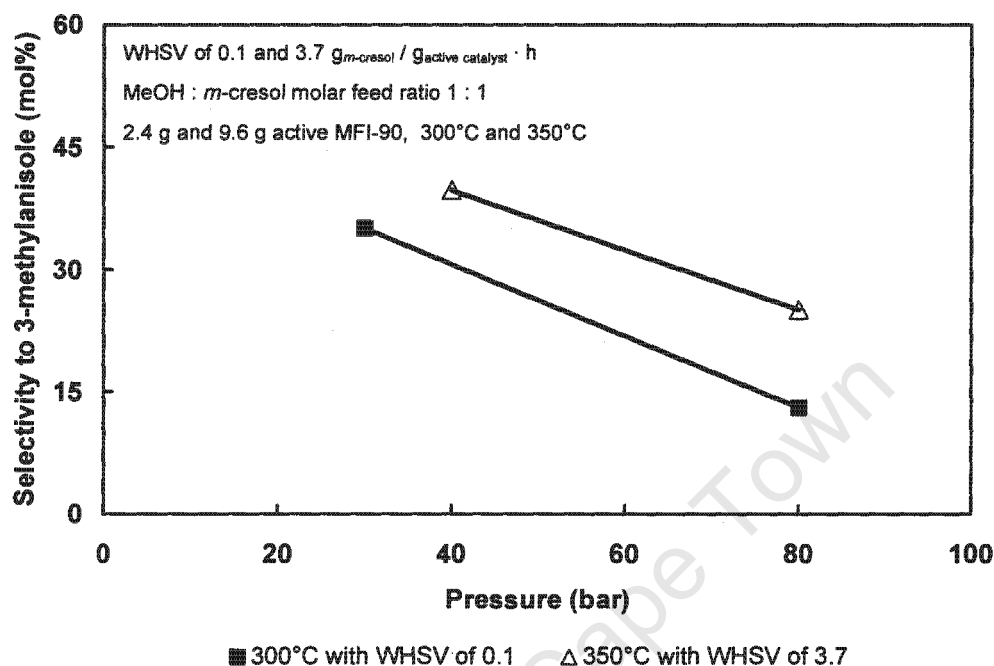


Figure 5-78: Comparing selectivity to 3-methylanisole versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.6 Selectivity to trimethylphenols (TMPs) at different reaction pressures

Figure 5-79 shows selectivity to trimethylphenols at 40 and 80 bar over MFI-90. Selectivity to trimethylphenols increased at increased reaction pressure.

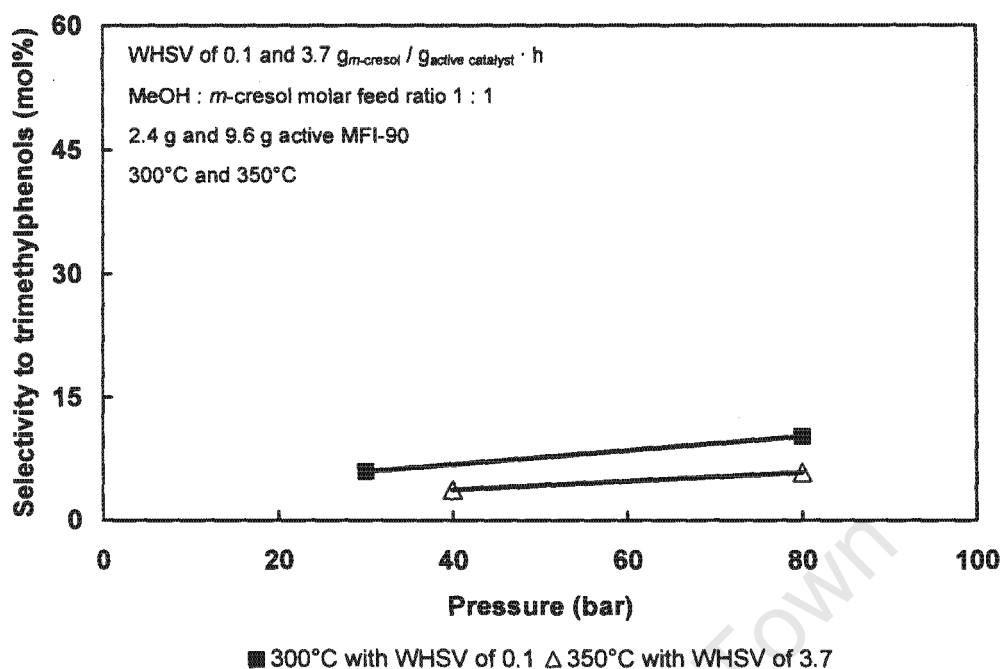


Figure 5-79: Comparing selectivity to trimethylphenols versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.7 Selectivity to "others" at different reaction pressures

Figure 5-80 shows selectivity to "others" at 40 and 80 bar over MFI-90. Selectivity to "others" increased at increased reaction pressure. Selectivity to "others" was at a level higher than the selectivity to TMPs (figure 5-79).

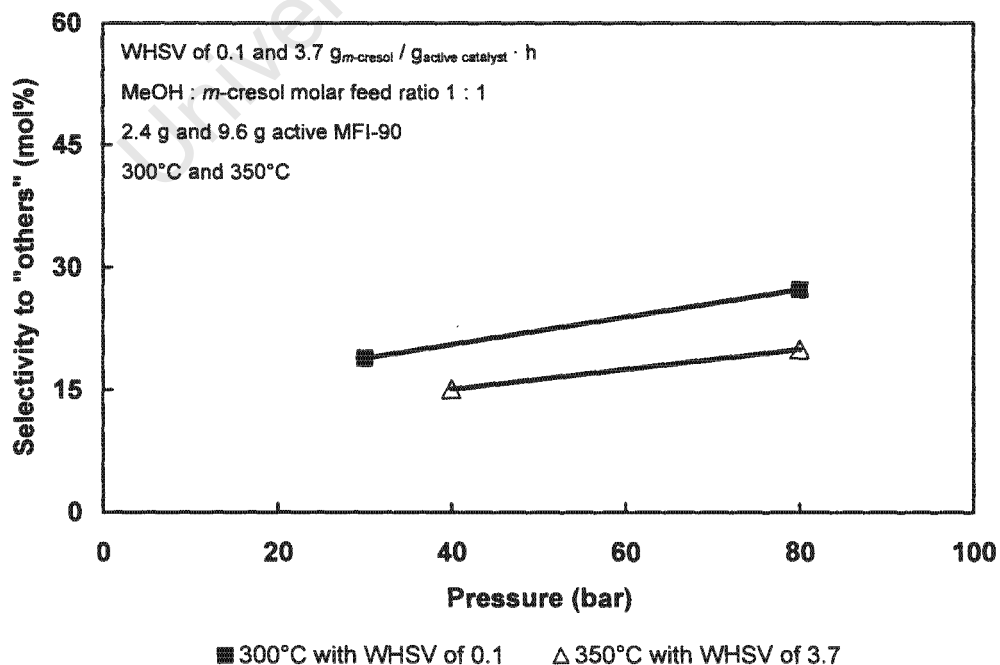


Figure 5-80: Comparing selectivity to "others" versus reaction pressure for *m*-cresol methylation over MFI-90

5.5.2.8 Selectivity to 2,5-, 3,4- and 2,3-xylenol at different reaction pressures

Figure 5-81 shows selectivity to 2,5-xylenol at 40 and 80 bar over MFI-90. Selectivity to 2,5-xylenol also increased at higher reaction pressure (14.1 and 14.7 to 17.0 and 16.4 respectively, figure 5-81), but not as steep as the increase in selectivity to 3,4-xylenol (figure 5-82).

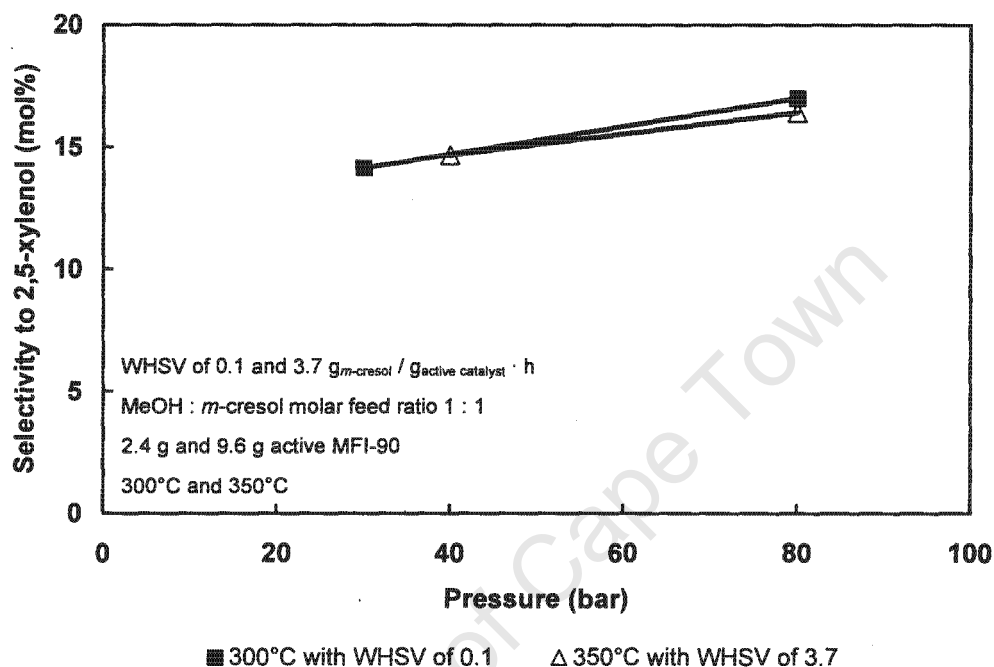


Figure 5-81: Comparing selectivity to 2,5-xylenol versus reaction pressure for *m*-cresol methylation over MFI-90

Figure 5-82 shows selectivity to 3,4-xylenol at 40 and 80 bar over MFI-90. The selectivity to 3,4-xylenol increased for higher reaction pressure. The increase observed was from 14.0 and 15.1 mol % to 19.6 and 19.4 mol % respectively (for reactions at 300°C and 0.1 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$ and 350°C and 3.7 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$).

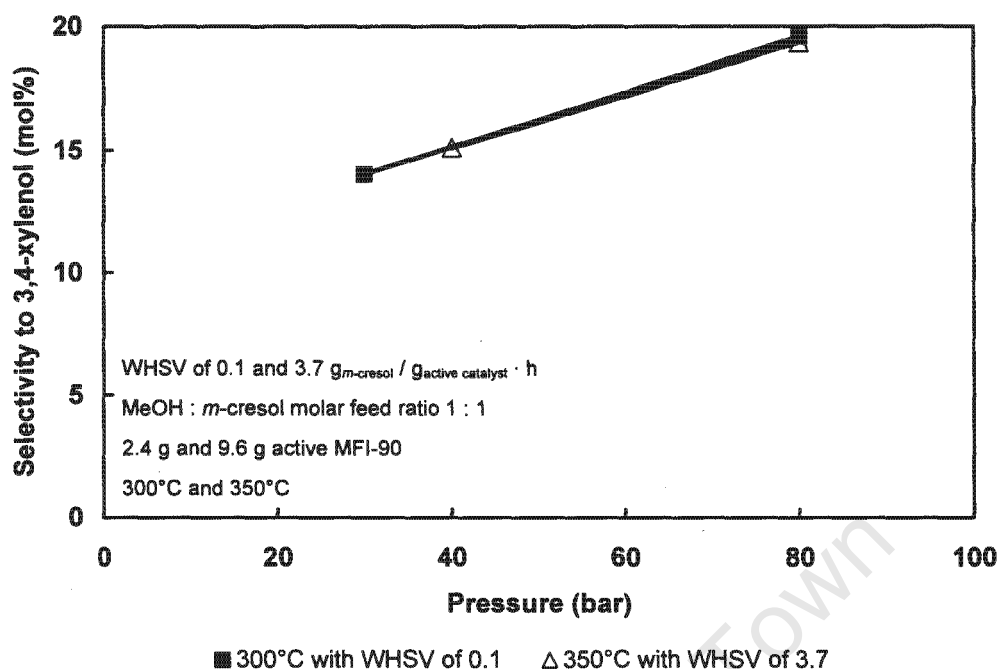


Figure 5-82: Comparing selectivity to 3,4-xylene versus reaction pressure for *m*-cresol methylation over MFI-90

Figure 5-83 shows selectivity to 2,3-xylene at 40 and 80 bar over MFI-90. Selectivity to 2,3-xylene did not vary much, remaining relatively constant over the range of pressure investigated.

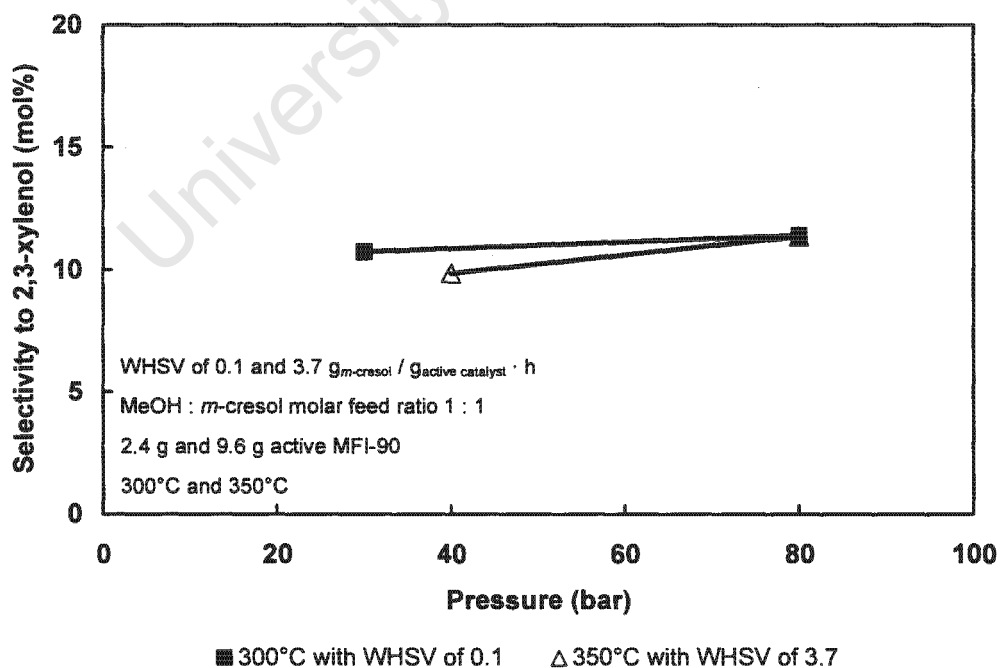


Figure 5-83: Comparing selectivity to 2,3-xylene versus reaction pressure for *m*-cresol methylation over MFI-90

Practically none of the isomers 3,5-, 2,4- and 2,6-xylene were produced under these conditions, therefore these data are not represented here (see appendix 2).

Note that the pressure effect data are influenced by the simultaneous, though quite moderate, increase in conversion with increasing pressure (see figure 5-82).

5.5.3 Methanol : *m*-cresol feed ratio effect

The feed ratio was varied to investigate whether selectivity and yield to desired xlenols varied with different feed ratios. Feed ratio experiments were conducted over MFI-90 at 300°C and 80 bar. Experiments were conducted at methanol : *m*-cresol molar feed ratios of 0.5, 1.0 and 2.0. However, for variation in feed ratio, pump rates of the feed mixture could not be fine tuned but were kept constant (see section 4.4.7 and appendix 6). Thus the WHSV with respect to *m*-cresol varied to some extent with change in feed ratio.

5.5.3.1 *m*-Cresol conversion at different feed ratios

Figure 5-84 shows conversion for varying feed ratio.

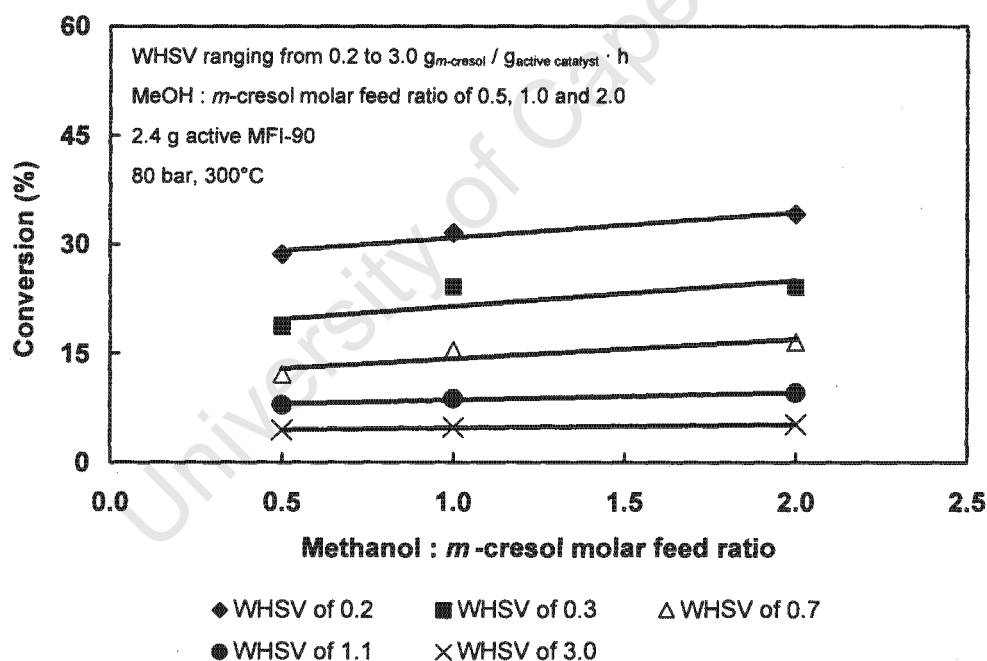


Figure 5-84: Conversion of *m*-cresol versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

The conversion achieved varied between 29 and 32 % at the lower most WHSV_{*m*-cresol} applies. However, the feed ratio variation has little direct effect on conversion.

5.5.3.2 Selectivity to total xylenols at different feed ratios

Figure 5-85 shows selectivity to total xylene isomers for varying feed ratio. For the methanol : *m*-cresol feed ratios investigated, selectivity to total xylenols was practically uninfluenced.

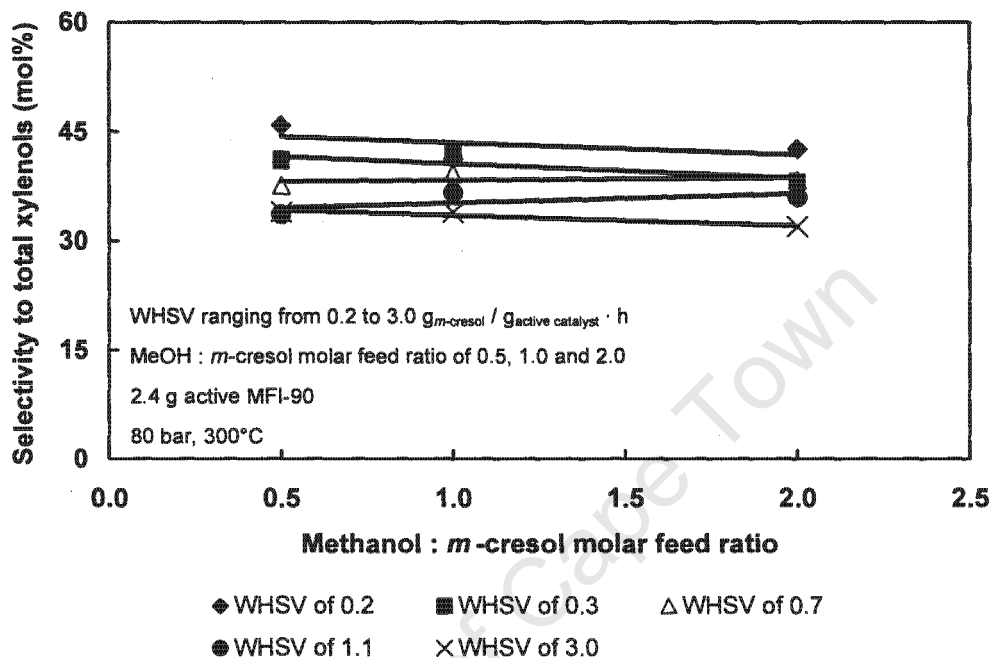


Figure 5-85: Selectivity to total xylenols versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

Showing no influence of variation of methanol : *m*-cresol feed ratio on selectivity holds for all product compounds or compound fractions investigated in this regard, see sections 5.5.3.3 to 5.5.3.10 and figures 5-74 to 5-81.

Practically none of the isomers 3,5-, 2,4- and 2,6-xylene, were produced under these reaction conditions, so the data are not shown.

5.5.3.3 Total xylenols yield at different feed ratios

Figure 5-86 shows yield of total xynolol isomers for varying feed ratio.

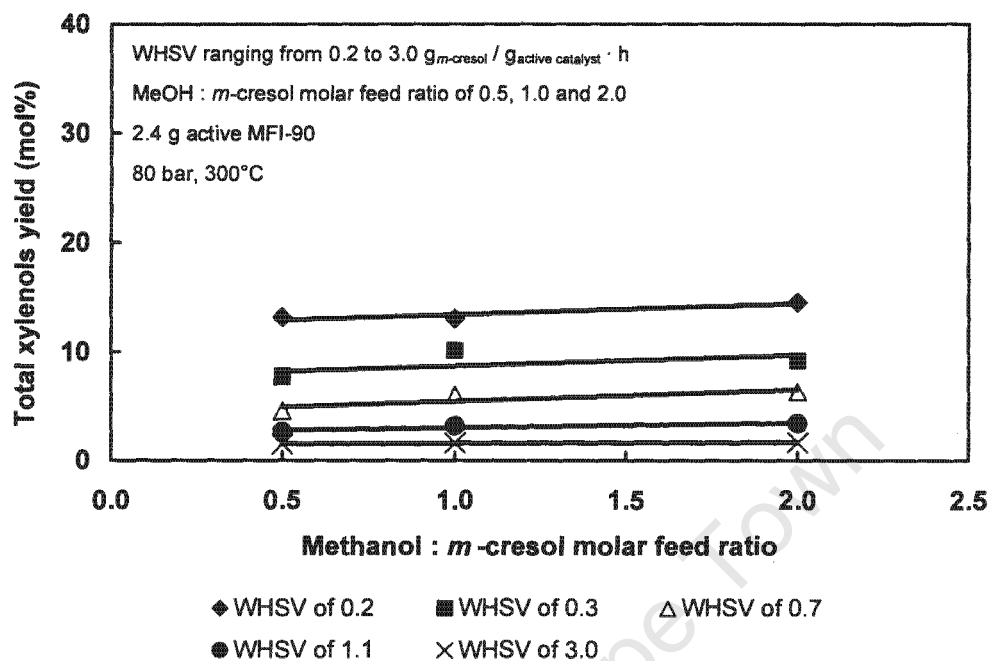


Figure 5-86: Total xylenols yield versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.3.4 Total xylenols within phenolic product at different feed ratios

Figure 5-87 shows xynolol isomers within phenolic product for varying feed ratio.

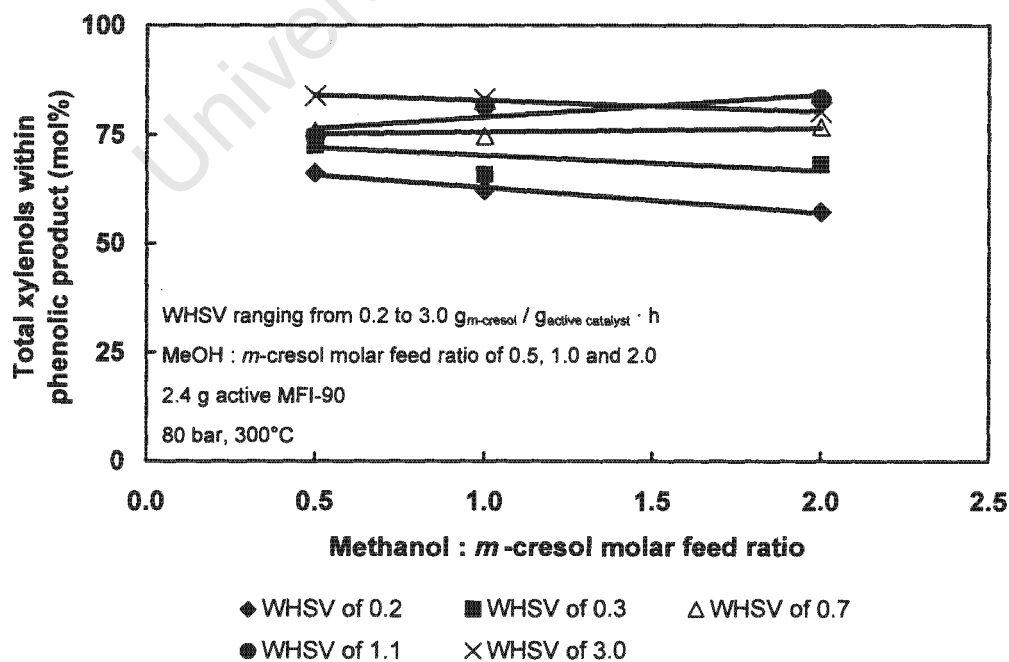


Figure 5-87: Proportion of total xylenols within phenolic product versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.3.5 Selectivity to 3-methylanisole at different feed ratios

Figure 5-88 shows selectivity to 3-methylanisole for varying feed ratio.

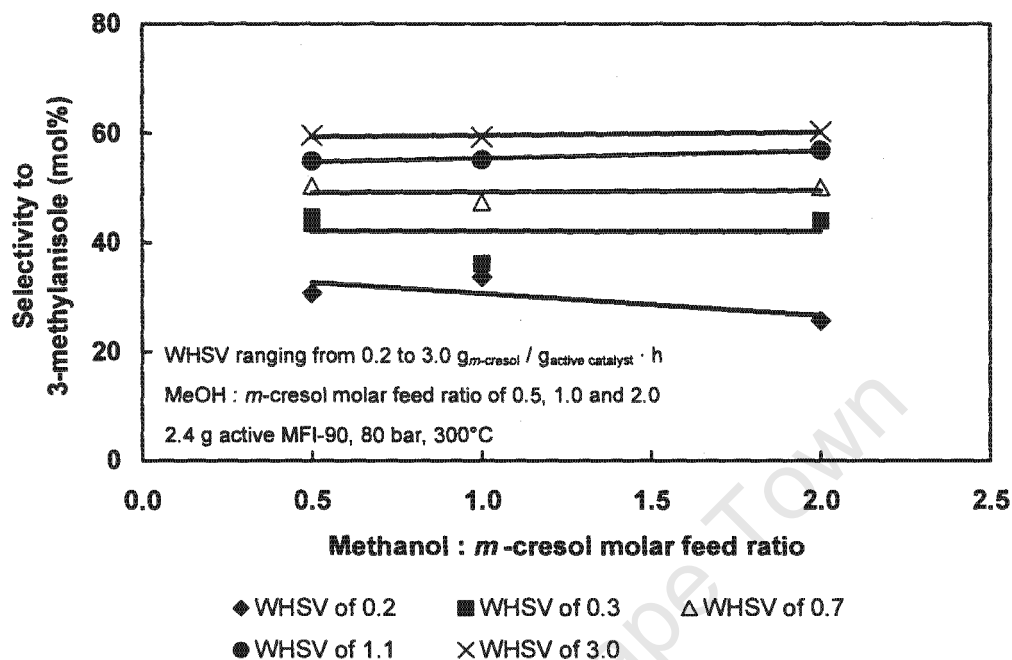


Figure 5-88: Selectivity to 3-methylanisole versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.3.6 Selectivity to trimethylphenols (TMPs) at different feed ratios

Figure 5-89 shows selectivity to trimethylphenols for varying feed ratio.

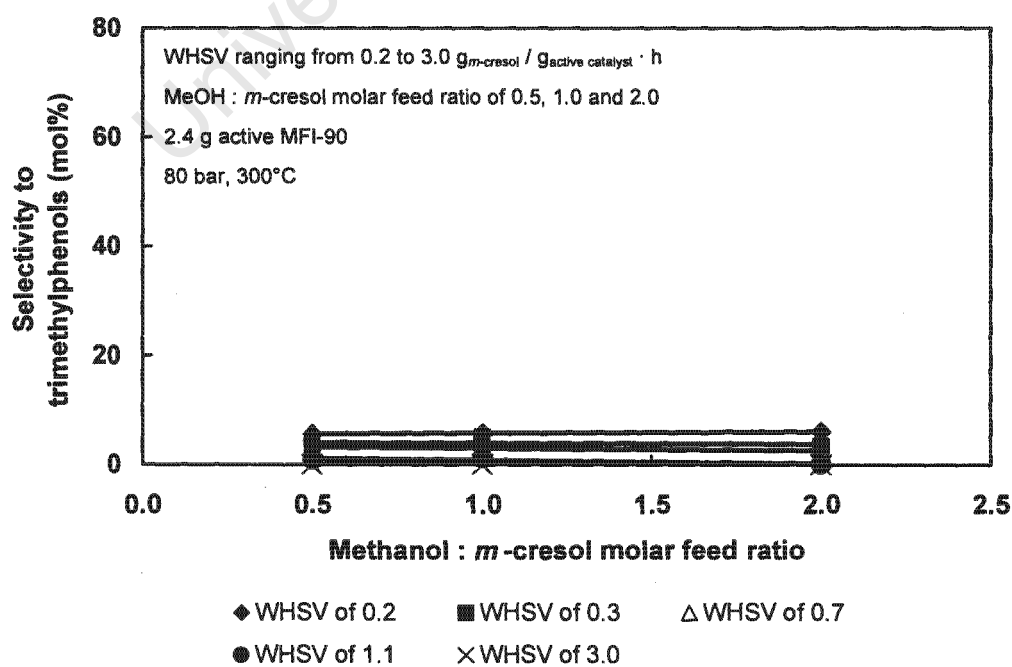


Figure 5-89: Selectivity to trimethylphenols versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.3.7 Selectivity to "others" at different feed ratios

Figure 5-90 shows selectivity to "others" for varying feed ratio.

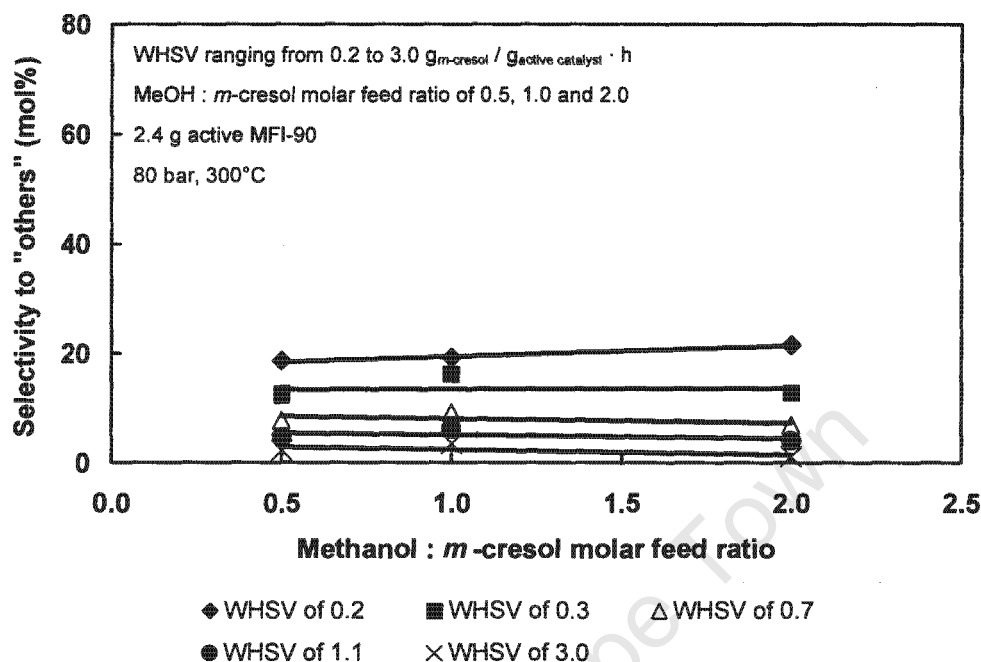


Figure 5-90: Selectivity to "others" versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.3.8 Selectivity to 2,5-, 3,4- and 2,3-xylenol at different feed ratios

Figure 5-91 shows selectivity to 2,5-xylenol for varying feed ratio.

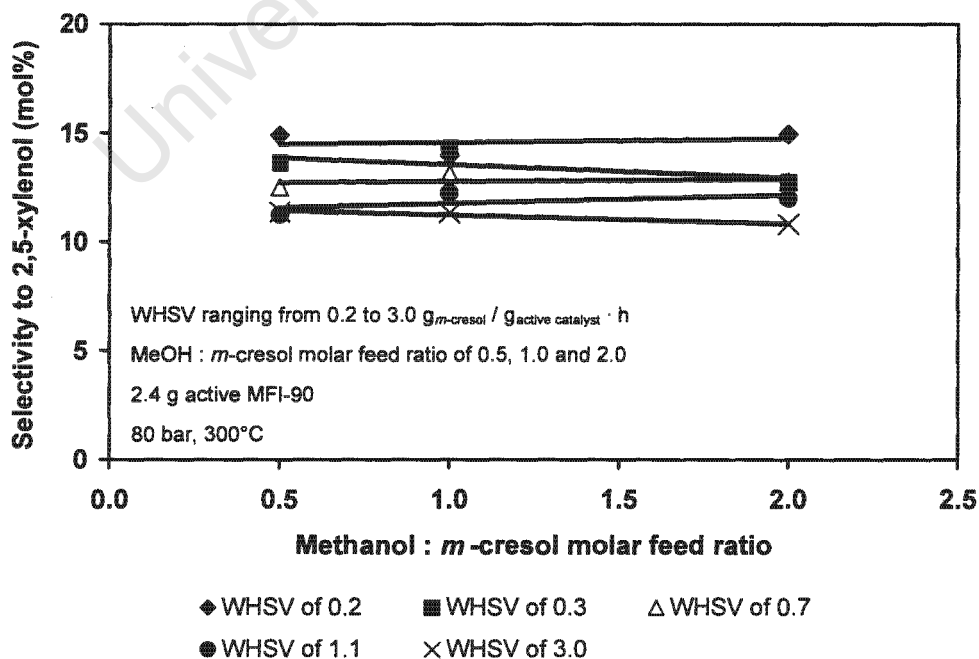


Figure 5-91: Selectivity to 2,5-xylenol versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

Figure 5-92 shows selectivity to 3,4-xylenol for varying feed ratio.

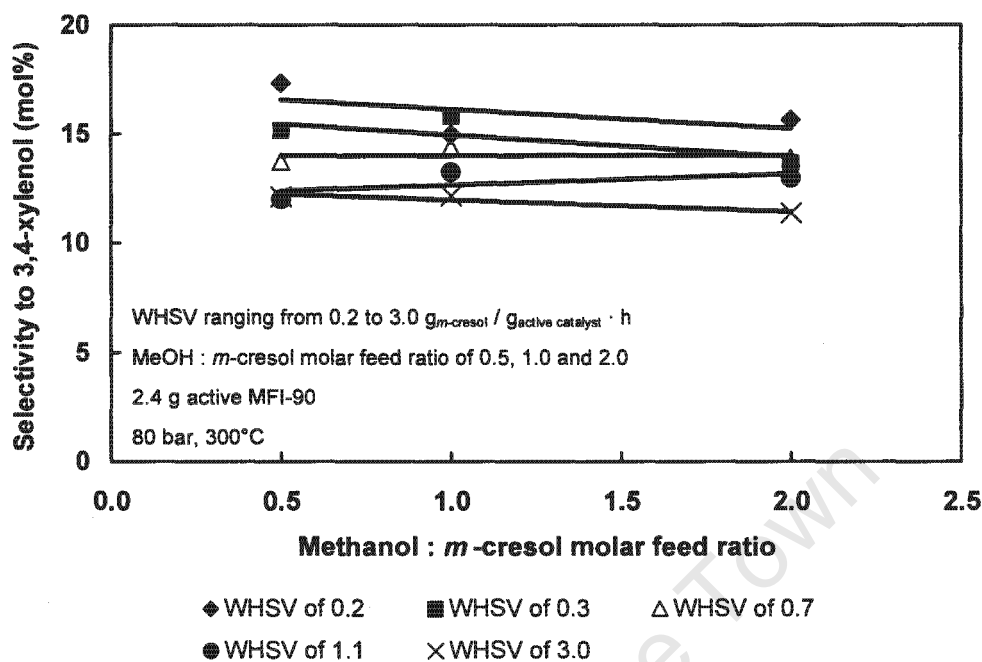


Figure 5-92: Selectivity to 3,4-xylenol versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

Figure 5-93 shows selectivity to 2,3-xylenol for varying feed ratio.

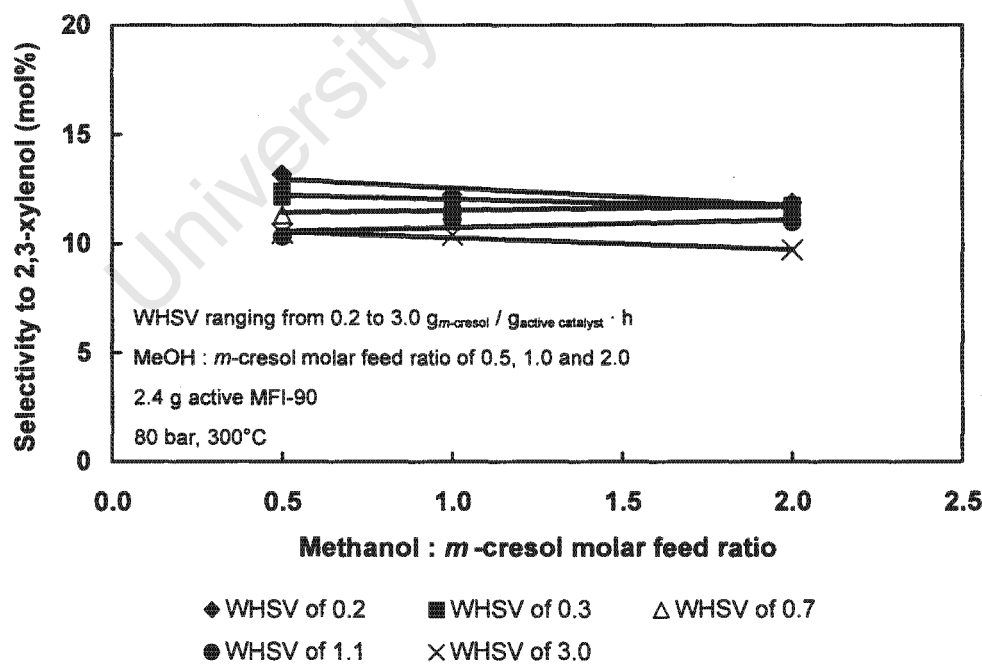


Figure 5-93: Selectivity to 2,3-xylenol versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different feed ratios

5.5.4 Effect of WHSV

5.5.4.1 The effects of variation in WHSV on the product distribution are shown in this section. Conversion at different WHSV

Figure 5-94 shows conversion for varying WHSV at different feed ratios.

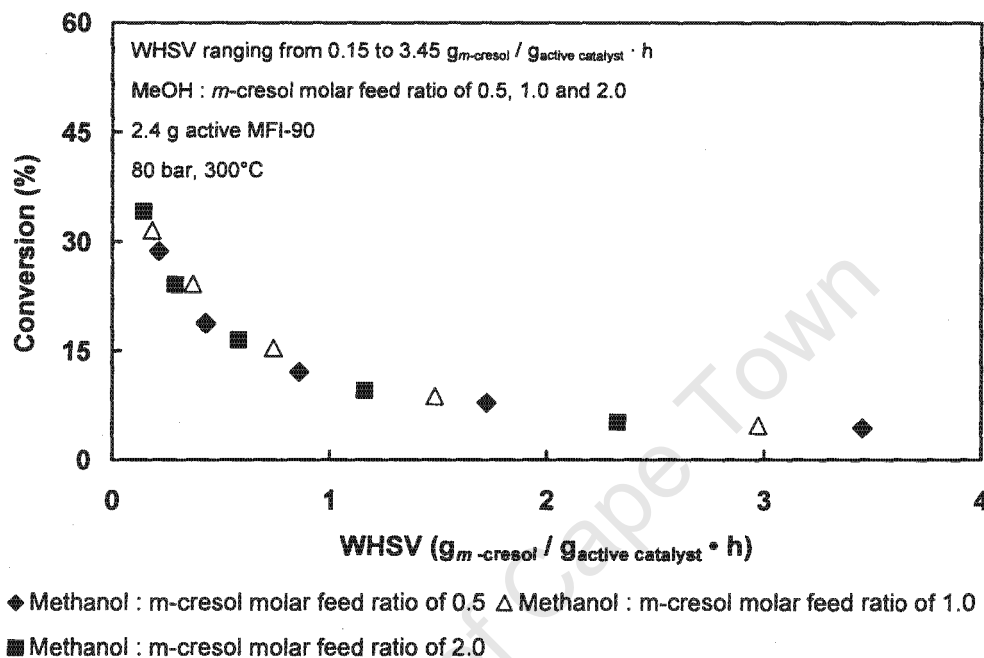


Figure 5-94: Conversion of *m*-cresol versus WHSV for *m*-cresol methylation over MFI-90

Conversion of *m*-cresol showed an exponential relationship with WHSV declining towards higher WHSV. Over the WHSVs investigated (0.2 to 3.5 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$) conversion ranged from 4 to 34 %.

5.5.4.2 Selectivity to total xylenols at different WHSV

Figure 5-95 shows selectivity to total xylene isomers for varying WHSV at different feed ratios.

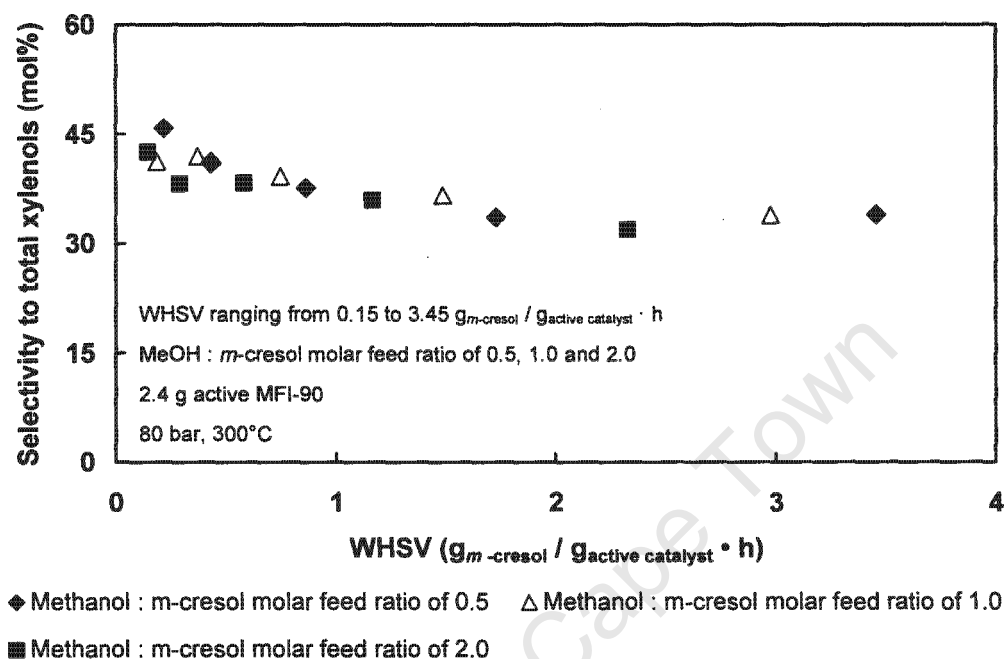


Figure 5-95: Selectivity to total xylenols versus WHSV for *m*-cresol methylation over MFI-90

Selectivity to total xylene was between 31 and 46 mol %. At low WHSV (i.e. higher conversion) selectivity to total xylene was a little higher as the xylene yield increasing steeply as well (see section 5.5.4.3 and figure 5-84).

5.5.4.3 Total xylenols yield at different WHSV

Figure 5-96 shows total yield of xylene isomers for varying WHSV at different feed ratios.

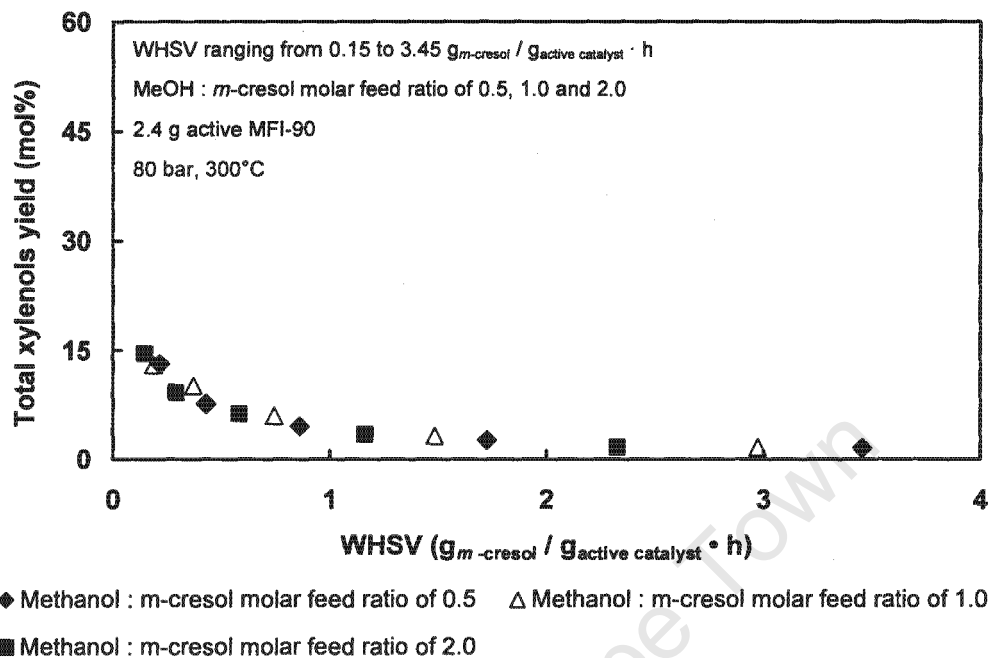


Figure 5-96: Total xylenols yield versus WHSV for *m*-cresol methylation over MFI-90

5.5.4.4 Total xylenols within phenolic product at WHSV

Figure 5-97 shows proportion of xylenols within phenolic product for varying WHSV.

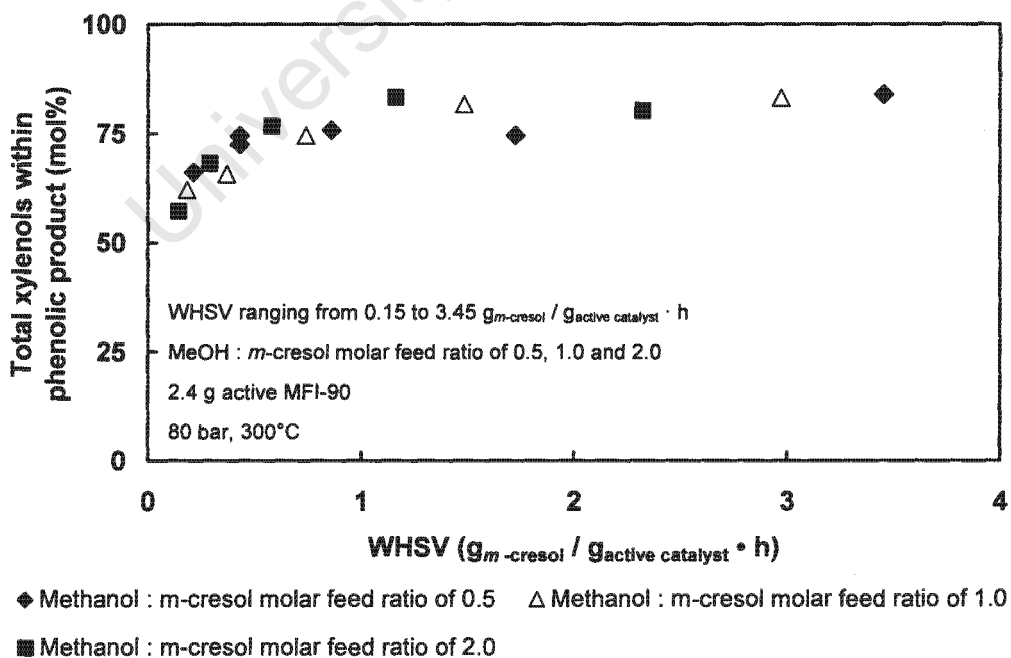


Figure 5-97: Proportion of total xylenols within phenolic product versus WHSV for *m*-cresol methylation over MFI-90

In contrast, the proportion of xylene isomers within phenolic product decreased from 80 mol % to 55 mol % at lower WHSV.

5.5.4.5 Selectivity to 3-methylanisole at different WHSV

Figure 5-98 shows selectivity to 3-methylanisole for varying WHSV at different feed ratios.

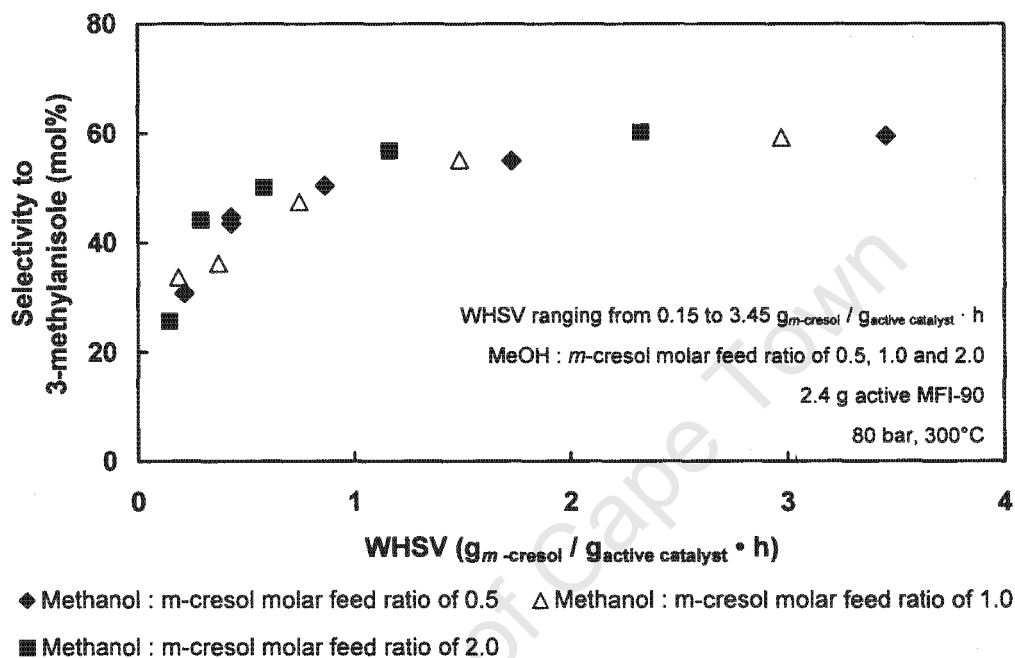


Figure 5-98: Selectivity to 3-methylanisole versus WHSV for *m*-cresol methylation over MFI-90

The selectivity to 3-methylanisole decreased significantly at lower WHSVs.

5.5.4.6 Selectivity to trimethylphenol isomers at different WHSV

Figure 5-99 shows selectivity to trimethylphenols for varying WHSV at different feed ratios.

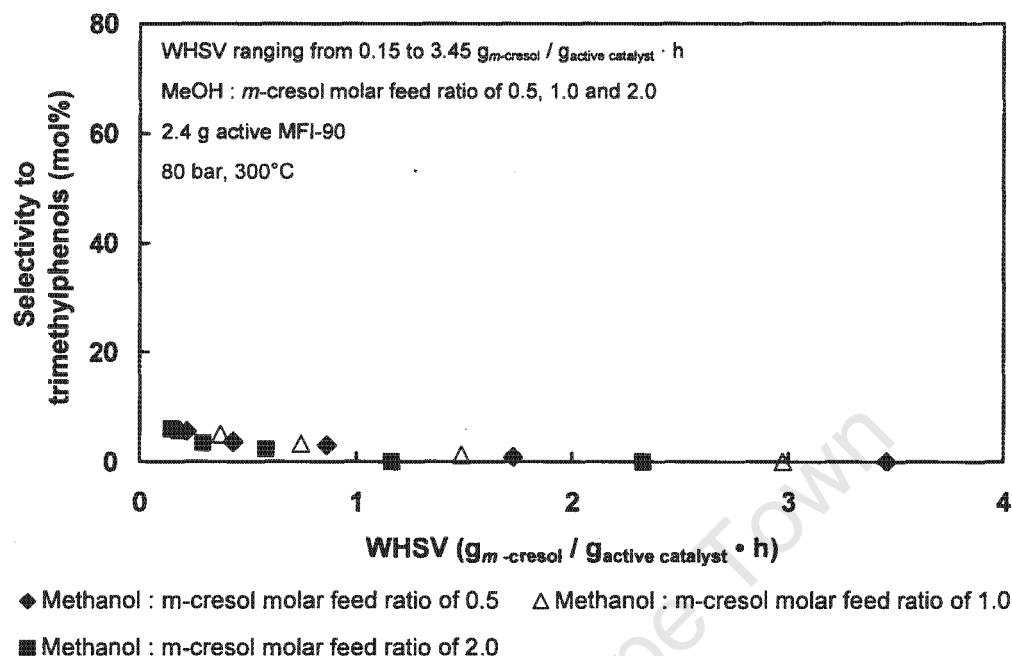


Figure 5-99: Selectivity to trimethylphenols versus WHSV for *m*-cresol methylation over MFI-90

At the lowest WHSV, selectivity to TMPs was about 7 mol %. This fell to zero at higher WHSV.

5.5.4.7 Selectivity to "others" at different WHSV

Figure 5-100 shows selectivity to "others" for varying WHSV at different feed ratios.

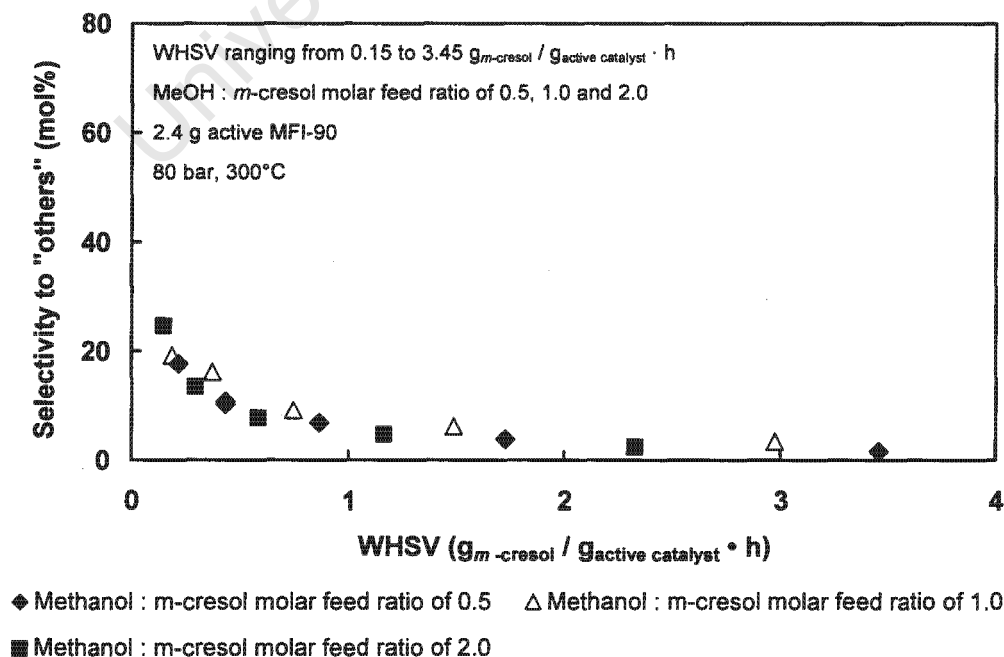


Figure 5-100: Selectivity to "others" versus WHSV for *m*-cresol methylation over MFI-90

Selectivity to “others”, which was around 24 mol % at low WHSV, fell to less than 5 mol % at higher WHSV.

5.5.4.8 Selectivity to 2,5-, 3,4- and 2,3-xylenol at different WHSV

Figure 5-101 shows selectivity to 2,5-xylenol for varying WHSV at different feed ratios.

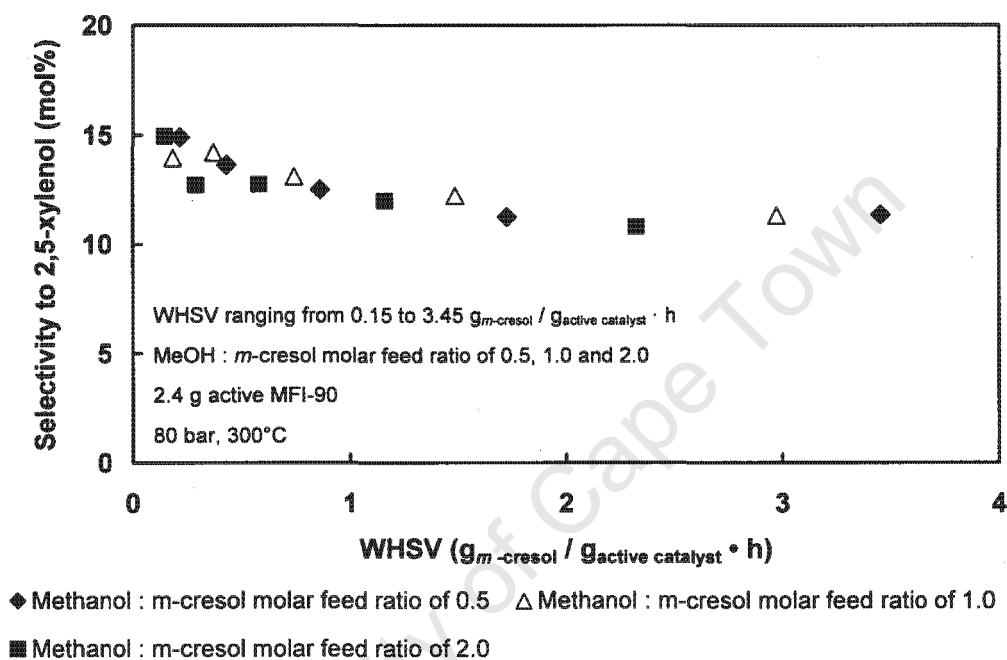


Figure 5-101: Selectivity to 2,5-xylenol versus WHSV for *m*-cresol methylation over MFI-90

Figure 5-102 shows selectivity to 3,4-xylenol for varying WHSV at different feed ratios.

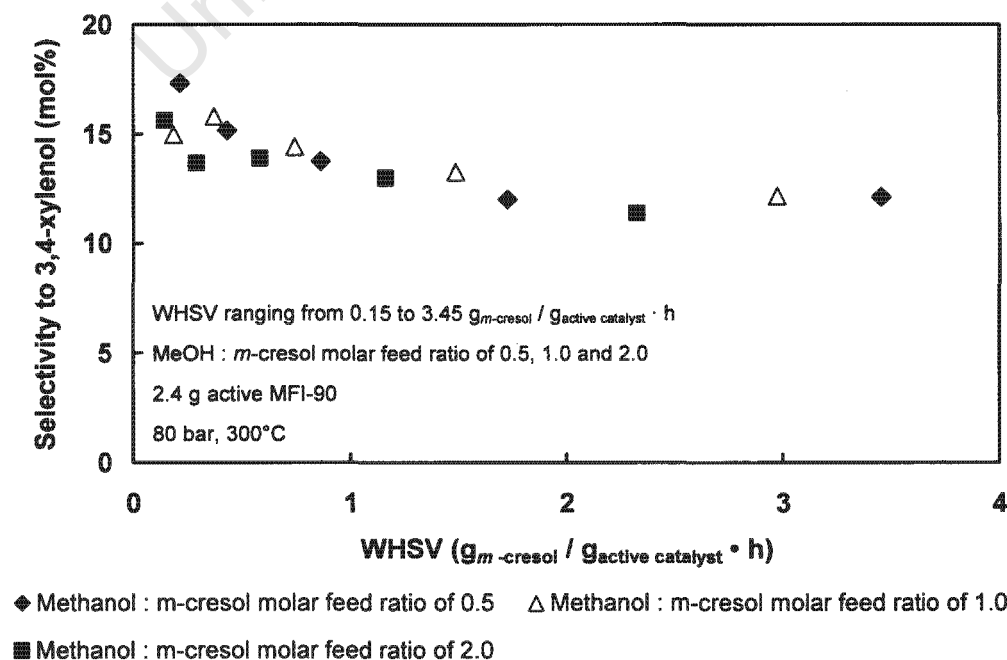


Figure 5-102: Selectivity to 3,4-xylenol versus WHSV for *m*-cresol methylation over MFI-90

Figure 5-103 shows selectivity to 2,3-xylene for varying WHSV at different feed ratios.

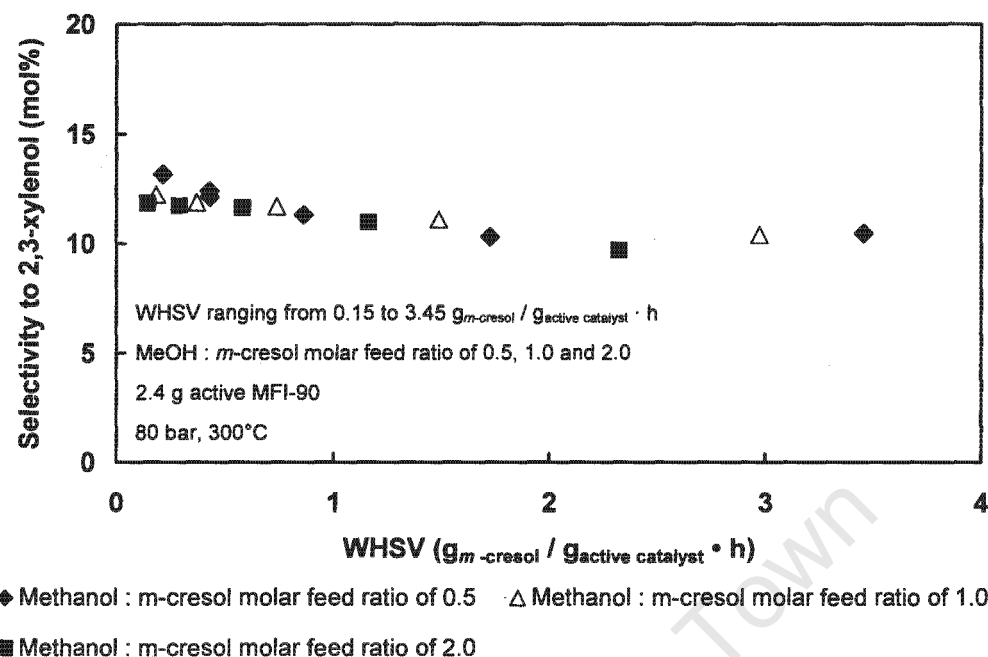


Figure 5-103: Selectivity to 2,3-xylene versus WHSV for *m*-cresol methylation over MFI-90

Of the individual xylene product isomers, the trends showing change in selectivity to each of these isomers with variation in WHSV that are very similar: all increasing slightly with decreasing WHSV (figures 5-89 to 5-90). Under these reaction conditions, yield of 3,5-, 2,4- and 2,6-xylene was very close to zero, thus this data is not represented here.

5.5.5 Reaction order

In order to determine the reaction activation energy, it was first necessary to test for the reaction order. Figures 5-104 to 5-106 have been drawn to test for reaction order of 0, 1 and 2, respectively.

Figure 5-104, obtained from assuming zero order shows that there is no linear relationship between conversion (*X*) and $\text{WHSV}_{m\text{-cresol}}$.

Figure 5-105, obtained from assuming first order, suggests that there could be a linear relationship between $\ln(1-X)$ and $1 / \text{WHSV}_{m\text{-cresol}}$, particularly for $1 / \text{WHSV}_{m\text{-cresol}}$ values of $< 3 \text{ g}_{\text{active catalyst}} \cdot \text{h} / \text{g}_{m\text{-cresol}}$.

Figure 5-106, obtained from assuming second order suggests that there could be a linear relationship between $X / (1 - X)$ and $1 / \text{WHSV}_{m\text{-cresol}}$, particularly for $1 / \text{WHSV}_{m\text{-cresol}}$ values of $< 3 \text{ g}_{\text{active catalyst}} \cdot \text{h} / \text{g}_{m\text{-cresol}}$.

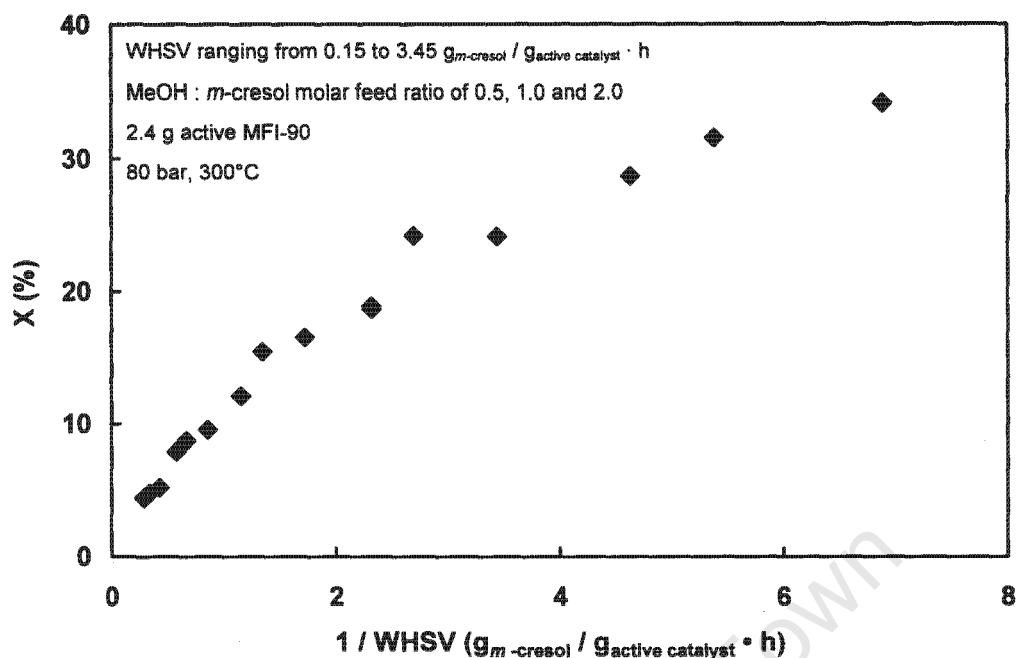


Figure 5-104: Plot of conversion (X) versus $1 / \text{WHSV}_{m\text{-cresol}}$ to test for reaction order of zero

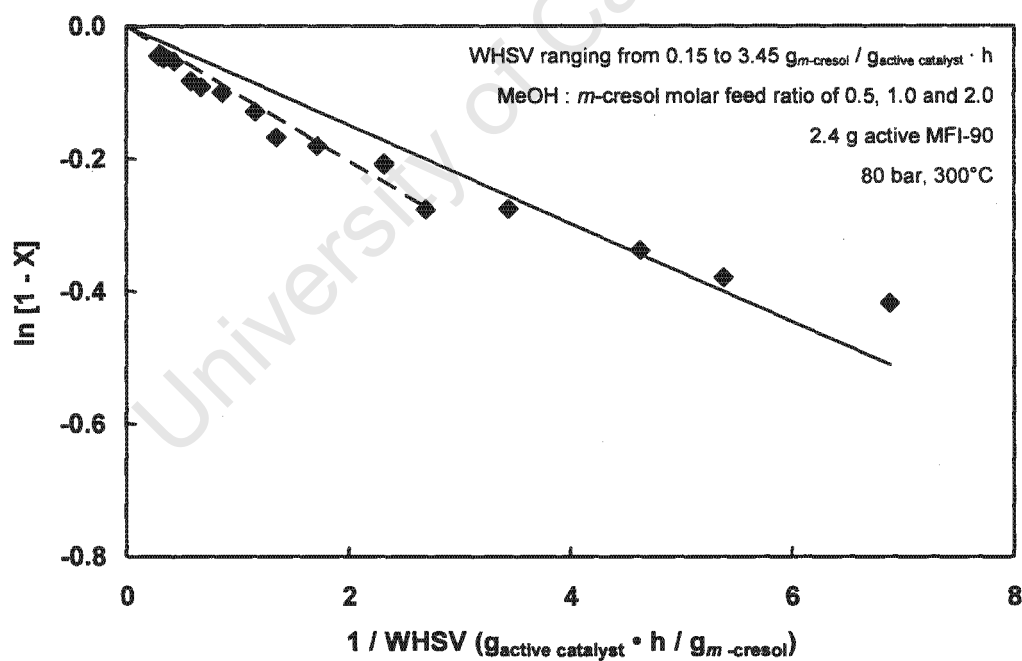


Figure 5-105: Plot of $\ln (1 - X)$ versus $1 / \text{WHSV}_{m\text{-cresol}}$ to test for reaction order of one. The trend lines have been forced through the origin.

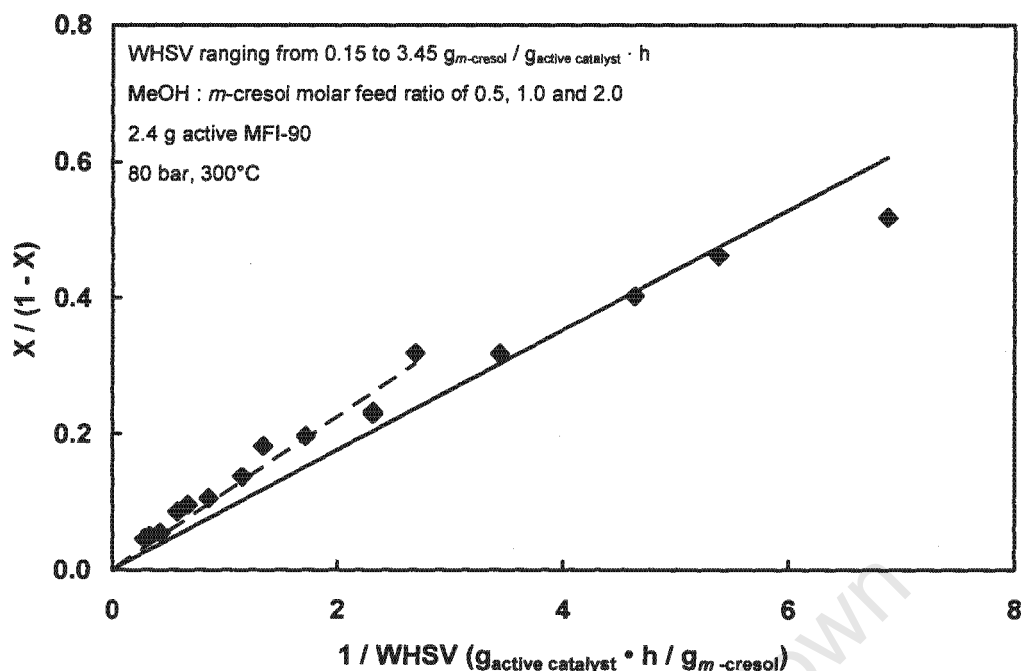


Figure 5-106: Plot of $X / (1 - X)$ versus $1 / \text{WHSV}_{m\text{-cresol}}$ to test for reaction order of two. The trend lines have been forced through the origin.

5.5.6 Summary of the effects of reaction conditions

The following general effects were found:

- Reaction temperature, 300 - 350°C: strong effects in every regard
- Reaction pressure, 30 – 80 bar: moderate effects
- Methanol : *m*-cresol feed ratio, 0.5 – 2.0: no effect
- $\text{WHSV}_{m\text{-cresol}}$, 0.2 – 3.5 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$: strong effect on conversion and yields, moderate effect on selectivities, except 3-methylanisole and "others", where the effect is strong.

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6. Discussion

6.1 Experimental Integrity

6.1.1 Isothermal zone

In order to compare activity of different catalysts and from different experimental campaigns it is important to ensure that the reactions are carried out in isothermal conditions or if this is not possible, accurately, with similar catalyst bed lengths and temperature profiles. During the different experiments it was necessary to continually monitor the temperature profile over the catalyst bed and, where necessary, manipulate the different heating zones to control the reaction temperature profile as shown in figure 4-5a and b. Thus catalyst bed temperature profiles were similar for each experiment. Figure 4-6 shows the temperature profile down the reactor during two different experiments, CM D3 and CM D4. The variation average temperature over the isothermal region was less than 2°C.

6.1.2 Impurities in feed

GC tests of raw feed revealed that it contained small amounts (0.7 mol %) impurities, mainly *p*-cresol (see table 4-2). This was taken into account when conducting calculations. The results presented were adjusted to account for this discrepancy.

6.1.3 Blank experiments

A blank experiment at base case conditions and the respective pump rate, conducted to determine the proportion of reaction that occurred in the absence of any catalyst, showed a conversion of 0.7 % to mainly xylenols (0.4 mol %) and 3-methylanisole (0.3 mol %) (see table 5-2). Subsequent conversion and selectivity calculations were adjusted to account for this.

6.1.4 Sample stability

As it was not always possible to analyse samples immediately after they were drawn, some samples were left standing for up to 48 hours. There is a possibility that such a time lag between sample drawing and analysis may result in inaccurate sample analyses. Figure 5-1 shows the results for a sample that was analysed nine times over 125 hours on the shelf. Throughout this period the sample composition did not change appreciably.

Thus it is concluded that the time between sample drawing and analysis did not affect the GC result.

6.1.5 GC analyses reproducibility

Repeated GC analyses of a sample showed little deviation between results (table 4-9). The sample stability data shown in figure 5-1 further suggests that GC analyses, analysed over several days from the same sample, are also reproducible (see section 6.1.4). Thus results obtained from GC analyses can be compared with confidence.

6.1.6 Experimental reproducibility

Figure 5-6 shows the results from repeated experiments that were conducted to evaluate the extent of experimental reproducibility. The results obtained from duplicate runs over MFI-220 and BEA-150 (new charges of zeolite in every case, runs CM D2 and CM D3 for MFI-220 and runs CM D6 and CM D10 for BEA-150) show that the experiments can be reproduced at a reasonable level of accuracy (see section 5.1.4 for details). Thus results of methylation reactions obtained from different runs and conducted over different catalysts can be compared with confidence.

6.1.7 Catalyst stability and deactivation

A certain amount of catalyst deactivation was experienced, particularly during the initial stages of the reaction. To reduce coke formation the reaction pressure was controlled within an operation window of 30 – 80 bar for reaction temperatures of 300 – 400°C so that *m*-cresol remained in liquid phase (see figure 4-2). Where there is a mobile liquid phase, coke precursors, mainly formed through the conversion of methanol to olefins, may be washed off and transported away from the active catalyst sites. This can retard deactivation (Fletcher, 2003).

FER-20 experienced the greatest loss of activity with time-on-stream and stabilised only at the very low level of *m*-cresol conversion of < 15 % (see figure 5-3). This was expected as FER-20 has the narrowest pore structure out of the zeolites screened and, since the 8-membered ring channels can be ignored, effectively has a mono-dimensional pore system (see table 2-15). In contrast, BEA-150 showed the least catalyst deactivation and stabilised at high level of conversion (> 50 %) at base case experimental conditions (see figure 5-2). This was also expected as BEA-150 has the largest pore size of the screened zeolites and an open, 3-dimensionally interconnected pore system (see table 2-15).

It has been reported that shape selective properties of a zeolite can become more apparent with increased coking as the actual size of the pore narrows somewhat (Olson

and Haag, 1984 and Balsama *et al.*, 1984) or, more probably, that most pore mouths get plugged. However, it was difficult to determine whether this coke induced shape selective effect indeed occurred during runs as coking had effect on conversion and it was likely that any difference in product distribution was, at least in part, due to change in conversion.

6.1.8 Comparison with thermodynamic data

Xylenol isomer equilibrium distributions, as obtained experimentally by Pigman *et al.* (1954) and those calculated from the data supplied by Daubert *et al.* (1999) were compared with distributions obtained experimentally in this work (figures 5-7 and 5-73). The xylene isomer distributions achieved experimentally in this work differed significantly from the equilibrium distributions that were both obtained experimentally (by previous researchers) and those that were calculated. The results shown in figures 5-7 and 5-73 were obtained at between 19 % and 61 % conversion. Since the maximum conversion achieved in this series of experiments with 1 : 1 molar methanol to *m*-cresol feed ratio, was 71 % (see table 5-4), it is unlikely anyway that the distribution of xylene isomers obtained in this work was ever close to the thermodynamic equilibrium distribution.

No thermodynamic data were available for the trimethylphenol isomers in the sources searched.

6.2 Shape selective effects in xylenols fraction

To compare for possible shape selective effects, ratios of the kinetically preferred, primarily formed xylene isomers (2,5-, 3,4- and 2,3-xylene) were compared with distributions that were produced over non-shape selective, amorphous Siral-40 at base case conditions (see table 5-1). 3,5-Xylene, the fourth isomer that can be formed primarily, is not considered since its selectivity is clearly determined by the very low reactivity of the second *m*-position on the ring.

As mentioned previously, 2,5-xylene, being the slimmest isomer, should be the preferred product when produced in a geometrically constrained environment, such as a narrow, medium pore size zeolite channel. Formation of 2,3-xylene, being more bulky than 2,5- and 3,4-xylene, should be somewhat hindered as 2,3-xylene will experience increased resistance when diffusing within a narrow zeolite channel in comparison with 2,5- or 3,4-xylene. Thus, a significant increase in the selectivity of 2,5-xylene compared to the selectivity of 2,3-xylene, could suggest selective diffusion control, i.e. a product shape selective effect.

Although 2,5-xylene is slightly slimmer than 3,4-xylene, the difference is much smaller than the difference between 2,5- and 2,3-xylene. Any difference in the selectivity of 2,5-xylene compared with 3,4-xylene would indicate very strong product shape selective effects.

In comparing for shape selectivity, the pore diameters of the zeolites and structures of the channel system are important (see table 2-15). More detailed information is included in section 2.7.3).

The calculated thermodynamic ratios at 350°C presented in the selectivity figures (see below) have been plotted for purposes of comparison. Thermodynamic data for gas phase conditions was drawn from data given by Daubert *et al.* (1999), see appendix 1 for the full calculations. No relevant difference is expected between the gas phase and the liquid phase equilibrium of phenolics isomers as shown through comparison of experimental data collected to determine the equilibrium of the cresol isomers at 380°C, by Imbert *et al.* (2000) in gas phase and Fritsch *et al.* (2002) in liquid phase.

Figures 6-1 to 6-6 illustrate these comparisons of selectivity in the form of isomer ratios. Note that the comparison of ratios, in particular when the nominator and denominator values have opposite trends, is a very sensitive measure, able to indicate subtle effects.

This implies, however, that data scatter will be rather pronounced as well. The data shown in figures 6-1 to 6-6 was drawn from figures 5-13 to 5-30 in section 5.3.5 and appendix 2.

6.2.1 Ratio of 2,5- : 2,3-xyleneol

The average ratios of 2,5- : 2,3-xyleneol isomers formed over the catalysts tested at base case conditions are shown in figure 6-1.

It can be seen that for all catalysts the average ratio of 2,5- : 2,3-xyleneol achieved was considerably lower than the thermodynamic ratio of 4.96 (see figures 6-1 and 6-2) i.e. kinetically controlled, since these data are drawn from experiments in which the conversion was not too close to 100 % (see figure 6-2).

A comparison of 2,5- : 2,3-xyleneol isomer product ratios formed over the individual catalysts tested shows that amorphous Siral-40 (average ratio of 1.17) and zeolite BEA-150 (average ratio of 1.21) produced the lowest ratios. This ratio can be considered as representing the intrinsic selectivity over Brønsted acid sites in a high silica material that do not suffer from spatial restrictions, i.e. as a base case. Of the zeolites screened, BEA-150 has the largest pore diameters of 6.6 x 6.7 Å (see table 2-15).

MTW-100, another large pore zeolite with maximum pore diameter of 5.6 x 6.0 Å, but only a two-dimensional interconnected pore system, produced a slightly higher 2,5- : 2,3-xyleneol average ratio of 1.47 at similar *m*-cresol conversions as achieved over BEA-150 and Siral-40.

The ratio of 2,5- : 2,3-xyleneol formation observed over large pore zeolite MOR-90 was at 2.16, i.e. substantially greater than that seen over BEA-150, MTW-100 or Siral-40. MOR-90 has, effectively, a channel system involving one mono-dimensional wide channel (6.5 x 7.0 Å) (see table 2.15).

The medium pore zeolites, FER-20 (average ratio of 2.20 over maximum pore diameter of 4.2 x 5.4 Å), MFI-220 and MFI-90 (average ratios of 2.06 and 2.17, respectively, over maximum pore diameter of 5.3 x 5.6 Å) produced similar average ratios of 2,5- : 2,3-xyleneol but at lower *m*-cresol conversions. However, ratios did increase with increasing conversion (see figure 6-2). See table 2-15 for zeolite pore dimensions.

The question arises as to whether the above observations evidence of shape selective effects or not?

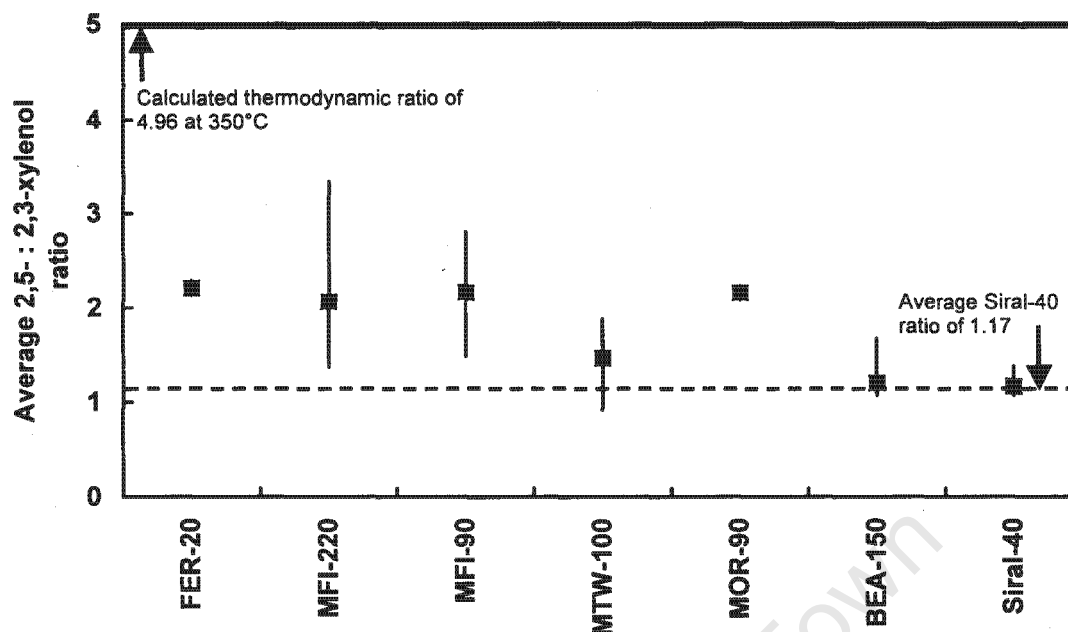


Figure 6-1: Comparison of average experimental distributions of 2,5- : 2,3-xyleneol ratios as produced over each catalyst screened at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). Results from repeated runs combined.

As reactions proceed towards completion (i.e. to higher conversion) the isomer distributions should begin to resemble the theoretical thermodynamic distribution more closely. The theoretical thermodynamic ratio of 2,5- : 2,3-xyleneol at 350°C is 4.96, which is much higher than the ratios achieved over any of the catalysts tested. Indeed, the data obtained from the reactions over MFI-90, MFI-220, MTW-100, BEA-150 and Siral-40 all suggest increasing 2,5- : 2,3-xyleneol ratio with increasing conversion. However, ratios obtained over the latter are almost constant, qualifying this catalyst again as a base case. This increasing ratio is in line with expectations. However, extending all of these series of data points to lower conversion appears to result in approximately the Siral-40 base case level of 1.17.

It is concluded that none of the above mentioned catalysts has any shape selective effects on the 2,5- : 2,3-xyleneol ratio. At low conversion the intrinsic selectivity of a Brønsted acid site is attained. Deviations towards equilibrium appear at high conversion.

However, the higher than “intrinsic” and constant ratios over FER-20 and MOR-90 at rather low conversion indicate that there may be some shape selective effect due to the narrower pores of FER-20 in the first case and the effectively one-dimensional pore systems of both these zeolites.

In studies comparing the shape selective effects of, amongst others, zeolites MFI-220 and BEA-150 in *m*-cresol isopropylation, Fletcher *et al.* (2003) showed that 6-isopropyl-3-methyl-phenol was produced at higher selectivity over MFI-220 than over BEA-150 at all *m*-cresol conversions achieved. Thus it appears that the other possible isopropylated isomers, where the isopropyl group is not in the opposite position to the given methyl group, have kinetic diameters that are very similar to that of the channels of MFI and indeed experience the shape-selective constraints of the narrow pore system of MFI. In contrast, while 3,4- and 2,3-xylenol are significantly smaller than the channels of zeolite MFI, the channels do not affect a shape selective effect.

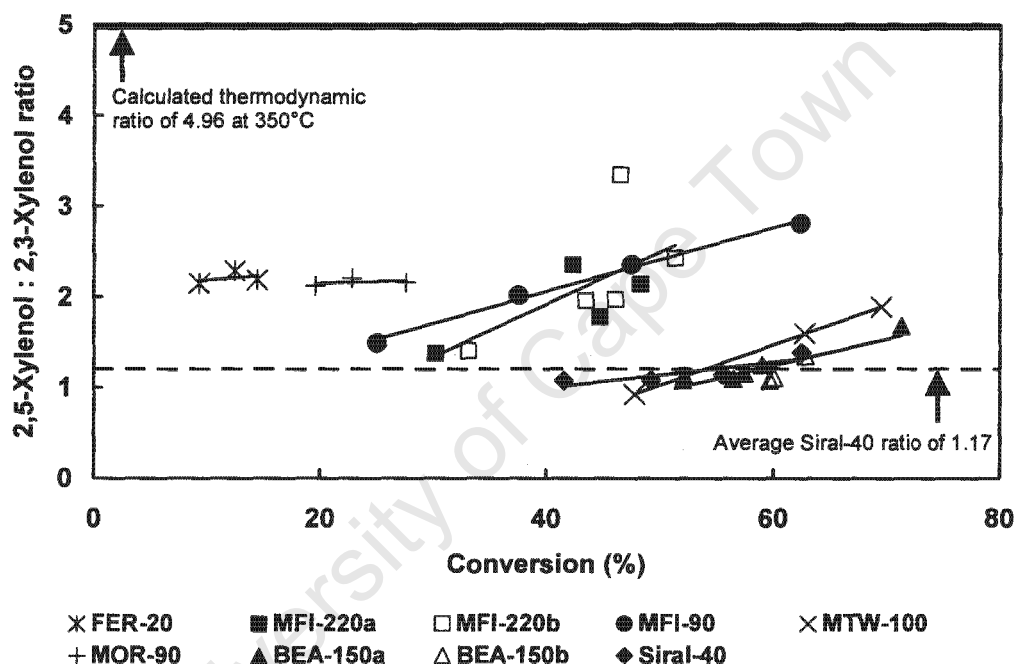


Figure 6-2: Comparison of experimental distributions of 2,5- : 2,3-xylenol ratios as a function of conversion at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

6.2.2 Ratio of 2,5- : 3,4-xylenol

Figure 6-3 shows the average ratios of 2,5- : 3,4-xylenol isomers formed over the catalysts tested, at base case conditions.

In general, the 2,5- : 3,4-xylenol ratios produced over each catalyst were very similar and apparently just scattering around the “intrinsic” ratio of 1.64, as obtained over Siral-40.

The data in figure 6-4 shows that, over each individual catalyst, the ratio of 2,5- : 3,4-xylenol is affected a little by conversion, however, in irregular manner, probably indicating that data scatter is the reason for the contradictory but only marginal trends and the

deviations from the “intrinsic” ratio. Apparently, neither shape selective nor other effects distinguish between these two isomers.

The only exception is over zeolite MFI-220, repeated, where a rather high ratio is obtained for conversion of around 30 %. This anomaly remains unexplained.

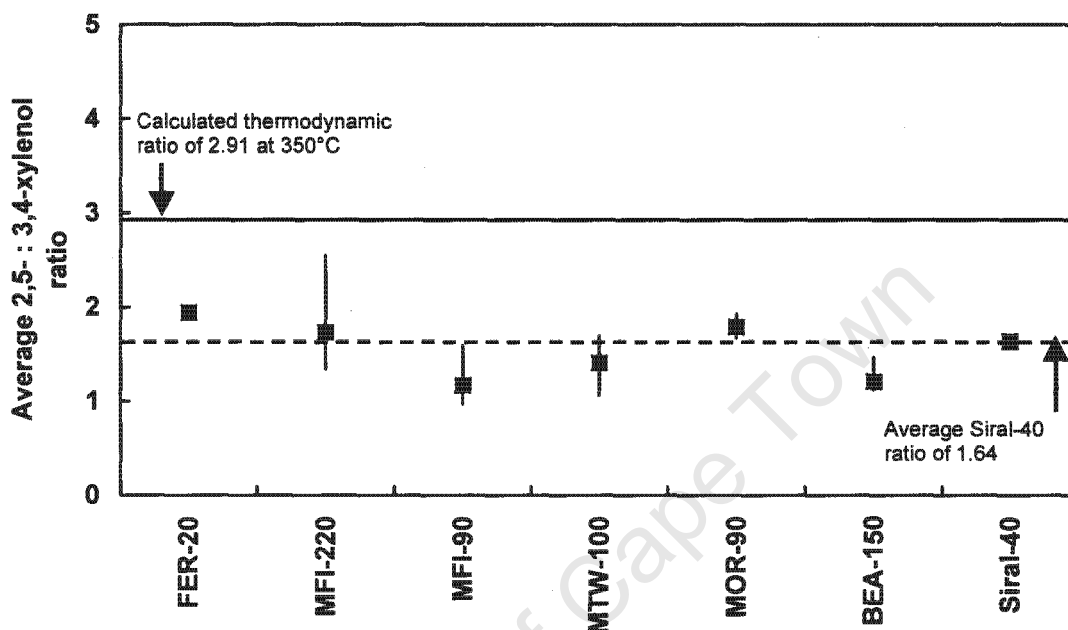


Figure 6-3: Comparison of average experimental distributions of 2,5- : 3,4-xyleneol ratios as produced over each catalyst screened at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). Results from repeated runs combined.

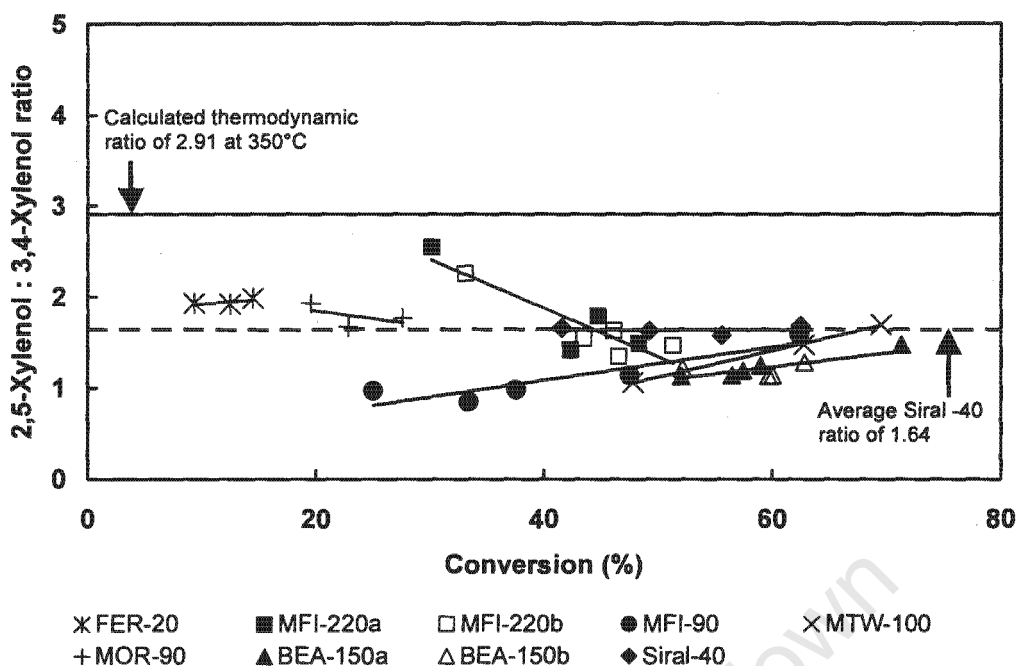


Figure 6-4: Comparison of experimental distributions of 2,5- : 3,4-xylenol ratios as a function of conversion at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

6.2.3 Ratio of 3,4- : 2,3-xylenol

Figure 6-5 shows the average ratios of 3,4- : 2,3-xylenol isomers achieved over the catalysts tested at base case conditions.

Wide pore zeolites, BEA-150 and MTW-100, produced average 3,4- : 2,3-xylenol product ratios of 0.99 and 1.02, respectively, which were slightly higher than that produced over Siral-40 (average ratio of 0.71). However, the differences were small.

A comparison of the data shown in figure 6-5 reveals that the highest 3,4- : 2,3-xylenol product ratio of 1.85 was achieved over MFI-90.

In general, the medium pore zeolites, FER-20 (average ratio of 1.13), MFI-90 (average ratio of 1.85) and MFI-220 (average ratio of 1.30) as well as wide pore zeolite MOR-90 (average ratio of 1.21) produced average 3,4- : 2,3-xylenol product ratios above that of Siral-40 and the large pore zeolites. However, as for the ratios of 2,5- : 2,3-xylenol, the values increase with conversion and the extrapolation to low conversion leads, essentially, to the "intrinsic" level, primarily produced by the Brønsted acid site, see figure 6-6. Thus, it seems that when compared with the results achieved over Siral-40, some shape selectivity was only indicated over FER-20 and MOR-90 that produced a still higher 3,4- : 2,3-xylenol ratio than that of Siral-40, at rather low conversion.

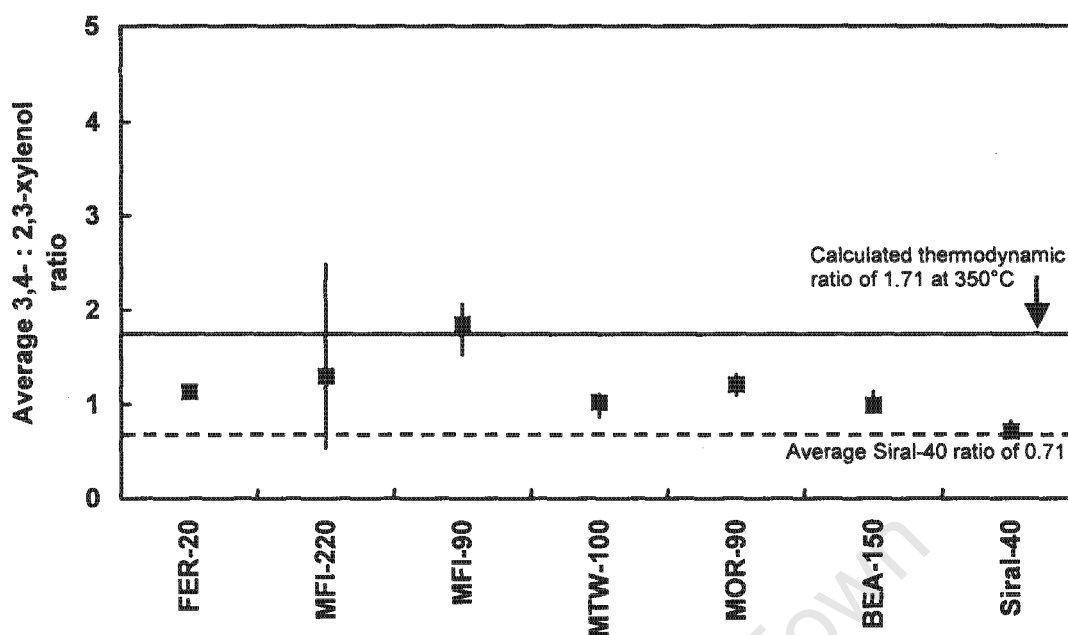


Figure 6-5: Comparison of average experimental distributions of 2,5- : 3,4-xylene ratios as produced over each catalyst screened at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999) . Results from repeated runs combined.

The almost flat trend observed for the MFI-90 (figure 6-6) at a rather high level (although there are only 4 data points, this range of data is very sensitive to experimental scatter) appears to indicate more towards the high activity of this catalyst towards secondary isomerisation than towards a shape selective effect.

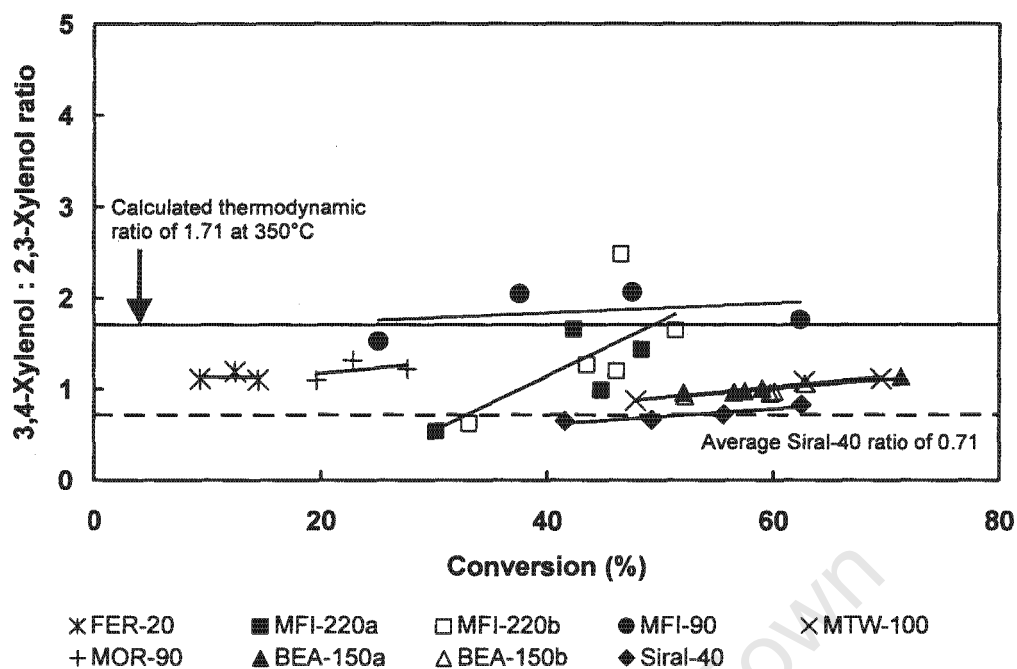


Figure 6-6: Comparison of experimental distributions of 2,5- : 3,4-xylenol ratios as a function of conversion at base case conditions, see table 5-1 (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

6.2.4 Summary of shape selective effects in xylenols fraction

In conclusion, catalysts BEA-150, MTW-100, MFI-90 and MFI-220 (of typical industrial zeolite make with small crystallite diameters around 0.1 – 0.2 μm) didn't show any shape selective effects on the methylation of *m*-cresol with methanol. At low conversion the product distribution matched the "intrinsic" selectivity of the Brønsted acid site, as obtained over amorphous silica-alumina (Siral-40) and at enhanced conversion the primary product was isomerised towards thermodynamic equilibrium.

Apparently narrow pore FER-20 and mono-dimensional pore MOR-90 influence some shape selective effect, showing ratios above the "intrinsic" value at rather low conversions, however, too weak to be of any potential industrial interest.

6.2.5 Shape selective effects in trimethylphenols fraction

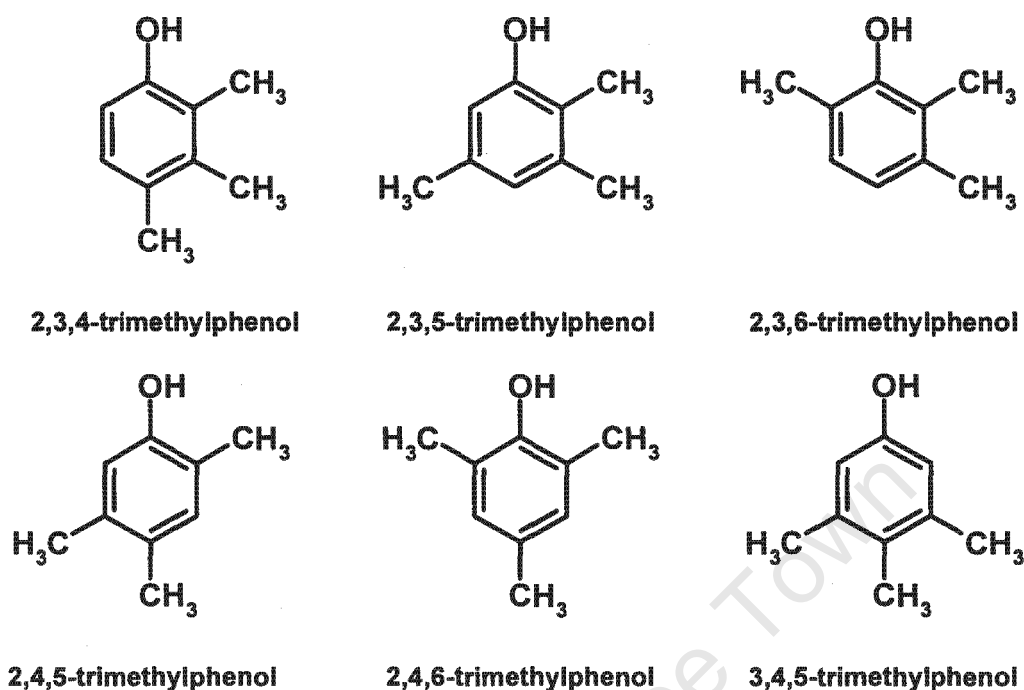


Figure 6-7: The six different trimethylphenol isomers

As summarised in section 5.3.7.7, differences in selectivities and yields of the trimethylphenols are not very pronounced over the different catalysts tested, except that 2,4,5-trimethylphenol, the slimmest of the trimethylphenol isomers, predominates over the MFI catalysts (see figure 6-7). This is analogous to the preference for 2,4,5-trimethylbenzene (pseudocumene) and 1,2,4,5-tetramethylbenzene (durene) in the aromatic C₉- and C₁₀-hydrocarbon fractions from methanol-to-gasoline conversion over H-ZSM-5 (MFI) the so called MTG process (Chang, 1983), which was clearly identified as a product shape selective effect.

As shown in sections 6.2.1 to 6.2.4, shape selectivity does not influence the xylenols much, but over MFI there is clearly has an effect with the trimethylphenols (as shown in section 5.3.7.7).

6.3 Reaction pathways

The product distributions indicate two primary reactions, i and ii (figure 6-8) as can be derived from figures 5-9 and 5-11 (dashed lines). The various reaction steps, i through x, are discussed and explained in the following section.

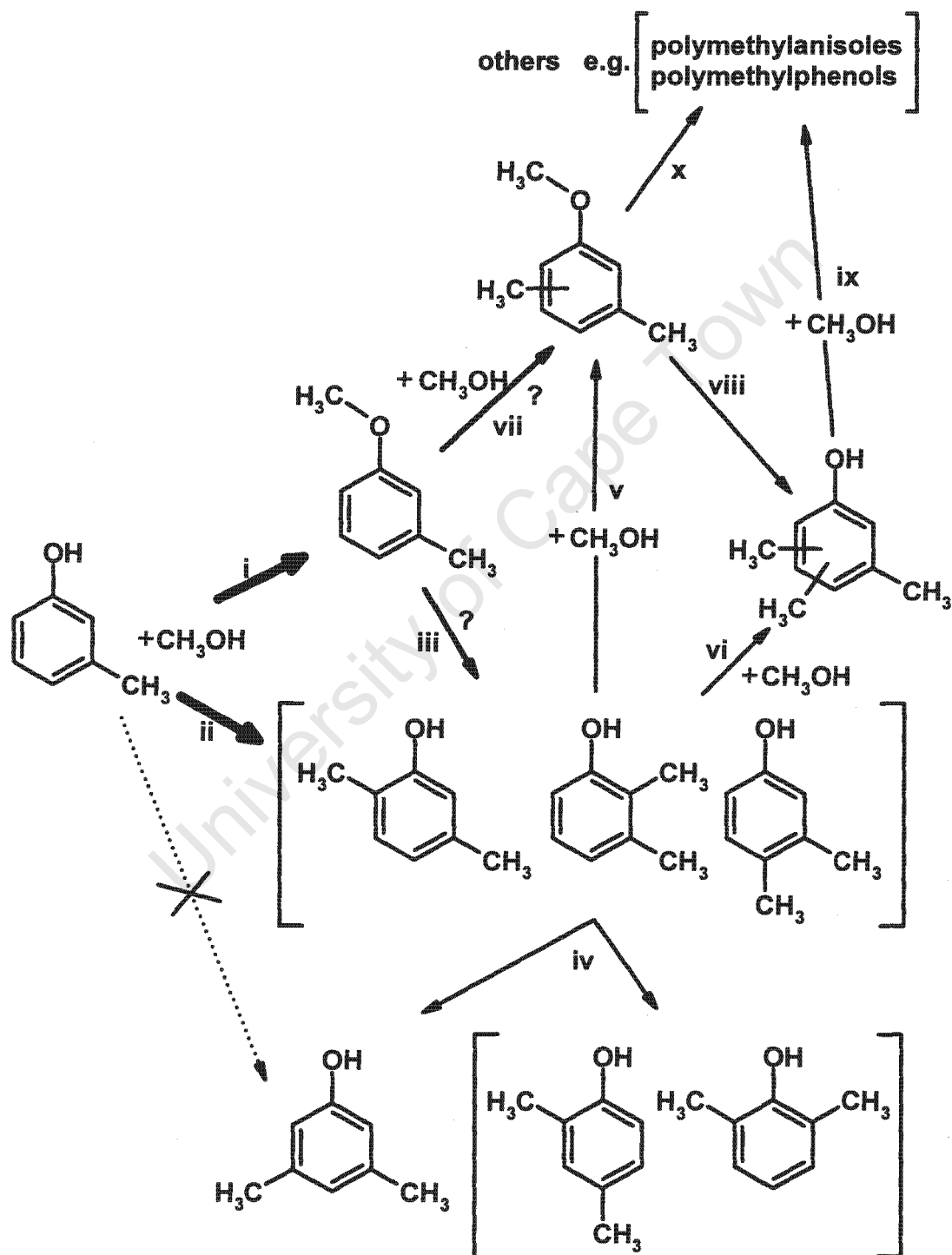


Figure 6-8: Possible reaction scheme explaining the distribution of products observed. The width of arrows indicates towards the relative contributions of the respective pathway. Question marks, "?", indicate that the relative impact of the two reactions could not be determined.

6.3.1 'O' alkylation of *m*-cresol

Reaction i, in figure 6-8, represents 'O' alkylation, by methanol, which results in the formation of 3-methylanisole (see section 2.8.5 and figure 2-19). At low conversions selectivity to 3-methylanisole was high, around 60 mol %, but decreased steeply as conversion increased (figure 5-10). Siral-40 yielded significantly higher amounts of 3-methylanisole than the zeolites, particularly at medium conversions (figure 5-11). Correspondingly the yield and selectivity to xyenols were significantly lower (section 6.3.2 and figures 5-8 and 5-9). This seems to reflect the low $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio of Siral-40, as weaker acid sites tend to favour 'O' alkylation (see sections 2.9.1 and 6.3.3).

Apparently, regarding data points over the entire range of conversion achieved, the yield of 3-methylanisole passes through a maximum with 3-methylanisole being formed as a primary product at low conversions but increasingly being consumed in secondary reactions as the conversion begins to increase (figure 5-11). Yield maxima were achieved between ca. 20 and 40 % conversion, depending on catalyst (see also section 6.3.4).

6.3.2 'C' alkylation of *m*-cresol

Reaction ii, in figure 6-8, represents 'C' alkylation, by methanol, which leads to the primary formation of the xylenol isomers, 2,5-, 3,4- and 2,3-xylenol. Comparison of results shows that 2,5-xylenol was preferred at lower conversions (see figures 5-13, 5-16, 5-19, 5-22 and 5-61).

There is an indication that the yield of 3,4-xylenol passes through a maximum at higher conversion (see figure 5-17). This could be due to the fact that 3,4-xylenol is a primary product and not very prevalent in the thermodynamic equilibrium xylenols fraction (see figure 5-61). As conversion increases, secondary reactions convert 3,4-xylenol into various secondary reaction products, mainly into the other xylenol isomers.

The results (figures 5-22 and 5-23) indicate that 3,5-xylenol, which could be a primary product (the dotted line in figure 6-8), is apparently not formed via primary ring methylation reaction. Thermodynamic calculations indicate that the proportion of 3,5-xylenol within the equilibrated xylenol mixture at 350°C would be 16.3 mol % and that the equilibrium 2,5- : 3,5-xylenol ratio would be 1 : 1.1 (figure 5-61). At conversions of less than 40 %, however, practically no 3,5-xylenol was formed (figures 5-22 and 5-23). Thus it is likely that 3,5-xylenol is not formed directly i.e. primarily via 'C' alkylation, but only secondarily, via 1,2-methyl shift isomerisation from the other primary xylenols. The lack of 3,5-xylenol formed via direct alkylation can be explained through the low reactivity of the *meta* positions on a

phenol ring. According to Sykes (1986), in *m*-cresol the respective position is *meta* to both the *p*- / *o*-directing hydroxyl group and *p*- / *o*-directing first methyl group.

6.3.3 Comparison of initial 'O' and 'C' alkylation selectivities

Figure 5-9 shows the average trend line (dashed) for all the data points obtained for xlenols yield. It clearly shows a straight line, which, as expected, (almost) meets the origin (the intersection with the origin has been forced).

In figure 5-11, another dashed line is given, derived from the former as the difference to the limit line $X = Y$. This line marks the limit for the sum of each of the products, including 3-methylanisole. As figure 5-11 suggests, at low conversion this line is the limit approached by the yield of 3-methylanisole, indicating that 3-methylanisole is the only primary product besides xlenols.

The percentage of each of the dashed trend lines in figures 5-9 and 5-11, relative to the limiting line $X = Y$, gives the initial or primary selectivities of 'O' and 'C' alkylation as follows:

- 'O' alkylation, primary, ca. 58 %
- 'C' alkylation, primary, ca. 42 %

So, at 350°C and the other base case conditions almost $\frac{2}{3}$ of the primary methylation steps take place on the 'O', i.e. of the two primary reactions i and ii, the former is clearly dominating at almost 1½ times the rate.

6.3.4 3-Methylanisole intra-molecular rearrangement

Reaction iii, in figure 6-8, represents the intra-molecular isomerisation of 3-methylanisole to either 2,3- or 2,5-xlenol, as discussed in section 2.8.5. At low conversions, selectivity to 3-methylanisole was almost 1½ times higher than selectivity to total xlenol products (section 6.3.3). As mentioned in section 6.3.1, the maximum 3-methylanisole yield was achieved at rather low conversion, between 20 and 40 %, and it began decreasing with increasing conversion (figure 5-11) while the yield of xlenols still increased (figure 5.9) along with yields of trimethylphenols (figure 5-31) and "others" (figure 5-46), which formed increasingly from about this point onwards. This could either mean that the xlenols do not react further (except by isomerisation), or that the consumption of xlenols is balanced by their formation from 3-methylanisole, i.e. a steady state intermediate selectivity. Unfortunately the number and quality of data does not allow a detailed kinetic analysis. Therefore no conclusion can be drawn towards the impact of the 3-methylanisole

rearrangement reaction and suggested whether a large proportion of xylene isomers are formed or not via the 3-methylanisole intra-molecular rearrangement pathway. However, the fact that the slope of the xylenes yield trend line became somewhat moderate at *m*-cresol conversions around 50 % could be expected if 3-methylanisole rearrangement would not play a role at all. This is not the case.

6.3.5 1,2-Methyl shift isomerisation of 2,3-, 2,5- and 3,4-xylene

Reaction iv, in figure 6-8, represents the isomerisation of the xylene isomers, 2,5-, 3,4- and 2,3-xylene that are formed as primary products, to xylene isomers 3,5-, 2,4-, and 2,6-xylene. As discussed in the beginning of section 6.2, practically no 3,5-xylene was produced below conversion of ca. 35 % (figures 5-22 to 5-24) that is, by direct ring alkylation and as a primary product. Also, selectivities to 2,4-xylene and 2,6-xylene were below 1 mol % for conversions below ca. 35 % (figures 5.25 and 5-28). Only above ca. 35 % conversion did selectivities to these three secondary isomers begin increasing, reaching a few percentage points at conversions up to 71 %. In conclusion, under conditions applied and maximum conversions achieved, 1,2-shift isomerisation did not play a major role.

6.3.6 'O' alkylation of 2,3-, 2,5- and 3,4-xylene, forming dimethylanisoles

Reaction v, in figure 6-8, represents alkylation of the 'O' atom to form dimethylanisole isomers. According to the mechanism discussed in section 2.8.5 the most likely isomers to form should be 2,5- and 3,4-dimethylanisole since their precursors, 2,5- and 3,4-xylene are the most abundant xylene isomers in the product, see figure 5-61. Also, since these are the most linear isomers of the dimethylanisoles, any possible shape selective effects would apply to the other, more bulky isomers. However, upon formation, 2,5-, 2,3- and 3,4-dimethylanisole may undergo similar internal rearrangement to that discussed in section 2.8.5 to form 2,3,6-, 2,3,4- and 2,4,5-trimethylanisole, respectively (reaction viii in figure 6-8). However, possible dimethylanisoles in the product were subsummarised with other compounds as "others" and not specifically identified in the chromatograms. Therefore, nothing can be said about the selectivity to dimethylanisoles. However, selectivities to "others" are about 25 % at > 50 % conversion and following the conclusions in section 6.3.3 about 'O' and 'C' alkylation, selectivity of dimethylanisoles might be higher than that of trimethylphenols, see section 6.3.6 and figure 5.31.

6.3.7 'C' alkylation of 2,3-, 2,5- and 3,4-xylenol forming trimethylphenols

Reaction vi, in figure 6-, represents the secondary alkylation of the xylenols with methanol to trimethylphenols (TMPs). However, the trimethylphenols can also form, to an unknown extent, by internal rearrangement of dimethylanisoles (section 6.3.8). Selectivity to trimethylphenols remained below 10 mol % for conversions of less than 35 % (see figure 5-31). At conversions of above 35 % selectivity to trimethylphenols increased to a maximum of 28 mol % (at 71 % conversion over BEA-150). The only trimethylphenol isomer that cannot form through methylation directly from the three primary xylenols, 2,5-, 3,4-, and 2,3-xylenol, is 2,4,6-trimethylphenol, with selectivities < 4 mol % (see figure 5-42), which is still significantly less than the selectivity of the most sterically constrained and very bulky 2,3,4-trimethylphenol isomer, which can form directly.

Section 5.3.7 (figures 5-34 to 5-45) contains graphs illustrating the selectivities to and yields of the different trimethylphenol isomers that were produced. Kinetically the preference for the trimethylphenol isomers is expected to be as follows:



The kinetic preference is at first influenced by the relatively low reactivity of the *meta* position, when compared to the *ortho* and *para* positions (see section 2.8.3 and Sykes, 1986) as well as steric hindrance (see sections 2.8.3 and 3.2).

In terms of shape selectivity, the most linear trimethylphenol isomer is 2,4,5-trimethylphenol. However, it is difficult to rank the other molecules for relative linearity and bulkiness, respectively. But indeed, shape selectivity is indicated through increased selectivity to 2,4,5-trimethylphenol over the MFI zeolites, see figures 5-40 and 5-41.

Thermodynamic data for these molecules was not given in the available sources so it was not possible to compare the thermodynamically controlled distributions of these isomers.

The product distributions recorded for methylation of *m*-cresol over the catalysts studied are given in table 5-5. The following ranking of trimethylphenol selectivities over the medium pore zeolites is apparent:



The following ranking of trimethylphenol selectivities over amorphous Siral-40 is apparent:



The most prominent difference is that Siral-40 produces 2,3,6-trimethylphenol at highest prevalence, while over the zeolites 2,4,5-trimethylphenol is produced at highest prevalence. Kinetically, 2,4,5-trimethylphenol would be expected at highest prevalence.

Although the thermodynamic distribution cannot be established due to lack of data, the trimethylphenol isomers, according to thermodynamic equilibration would be expected to rank as follows:



The isomers have been ranked for stability according to the following aspects:

- *meta* position side chains: where the presence of a *meta* group increases the thermodynamic stability
- steric hindrance: where increased steric hindrance corresponds with decreased thermodynamic stability (see sections 2.8.3 and 3.2)
- molecule symmetry: where increased symmetry, i.e. less permutations, corresponds with decreased thermodynamic stability

The phenomena of increased prevalence of 2,3,6-trimethylphenol over Siral-40 (see table 6-1) can possibly be explained by the fact that 2,3,6-trimethylphenol could be preferred thermodynamically compared with 2,4,5-trimethylphenol. Being uninfluenced by shape selective effects, the product distribution achieved over Siral-40 is probably slightly more representative of the thermodynamic distribution, although still heavily influenced by the kinetic constraints. It is interesting that, as conversion increased, the ratio of 2,4,5- : 2,3,6-trimethylphenol began increasing as well.

In ranking the thermodynamic stability of trimethylphenol isomers, 2,3,6-trimethylphenol was ranked ahead of 2,4,5-trimethylphenol (see above) although the difference is likely to be minor. The trend seen here appears to confirm this.

When comparing the ratios of 2,4,5- : 2,3,6-trimethylphenol produced over the different zeolites, it is apparent that much higher ratios were produced over MFI-90 than over any of the other zeolites (see table 6-1). This trend corresponds with the discussion in section 6.2.5.

Table 6-1: 2,4,5- : 2,3,6-Trimethylphenol ratios over different catalysts for different conversions achieved at base case conditions (see table 5-1). These values have been calculated from those in table 5-5.

	Catalyst						
	FER-20	MFI-90	MFI-220	MOR-90	MTW-100	BEA-150	Siral-40
15 %	1.1						
20 %				1.2			
40 %		2.4	1.0				0.5
50 %		2.5	1.9		1.0	1.2	0.6
60 %		2.6			1.1	1.3	0.7

6.3.8 'C' alkylation of 3-methylanisole, forming dimethylanisoles

Reaction vii, in figure 6-8, represents the 'C' alkylation of 3-methylanisole to dimethylanisole isomers. Since not individually detected for, dimethylanisole isomers were considered as "others" (see section 6.3.5). The dimethylanisole isomers that are most likely to form from the 3-methylanisole are 2,5-, 3,4- and 2,3-dimethylanisole corresponding to the reactivity of the available positions on the ring. For more details, see section 6.3.2. It is most probable that "others" comprise mostly dimethylanisoles, see section 6.3.6 for details.

6.3.9 Dimethylanisole intra-molecular rearrangement

Reaction viii, in figure 6-8, represents internal rearrangement of dimethylanisoles to trimethylphenols, analogous to the rearrangement of 3-methylanisole (reaction iii in figure 6-8 and section 6.3.4).

6.3.10 Formation of "others"

Reactions ix and x, in figure 6-8, represent further alkylation of trimethylphenols and dimethylanisoles with methanol. Products that could have formed include tetramethylphenol isomers and trimethylanisole isomers. These products were not identified as such but are included in the "others". It is most probable that "others" comprise mostly dimethylanisoles, see section 6.3.6 for details.

6.4 Reaction parameter effect

All experiments conducted to investigate effect of reaction conditions on the methylation of *m*-cresol were conducted over a single type of catalyst, MFI-90. Usually a single parameter was varied while the other ones were kept at base case values (table 5-1). The experiments on condition effects comprised three series (each with a new load of fresh catalyst), namely CM D4, CM D12 and CM D13 (see table 5-4 and appendix 2).

6.4.1 Effect of space velocity and conversion

In these experiments $WHSV_{m-cresol}$ was changed through manipulation of the feed rate and the composition of the feed mixture. When space velocity was reduced the trivial effect of increasing conversion appears (figure 5-94) along with increasing xyleneol yield (figure 5-96).

Figures 5-94 to 5-103 show conversion and selectivities to various products versus $WHSV_{m-cresol}$. It can be clearly seen that changing the $WHSV_{m-cresol}$ has a large impact on conversion and selectivity to products. The change of product selectivities is shown in figure 5-95 and figures 5-98 to 5-103. These figures confirm and detail the conclusions drawn about the reaction network (section 6.3 and figure 6.8), namely, with decreasing $WHSV_{m-cresol}$ (and increasing conversion) there is:

- a slight increase in total xylenols selectivity (figure 5-95), confirming that the xylenols are not only a primary alkylation product but also, to some extent, produced by an additional, secondary pathway, which is the internal rearrangement of 3-methylanisole
- the very same pattern for the selectivity of the three individual primary isomers (figures 5-101 to 5-103 and figure 6-9a). The latter directly compares.

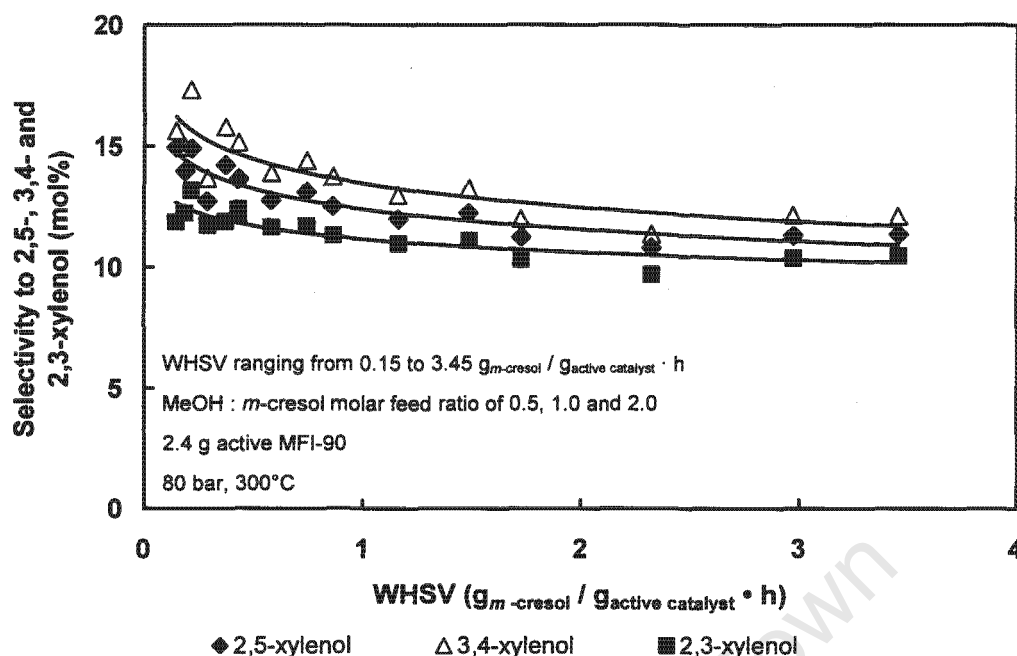


Figure 6-9a: Selectivity to individual primary xylene isomers, 2,5-, 3,4- and 2,3-xylene for variation in $\text{WHSV}_{m\text{-cresol}}$

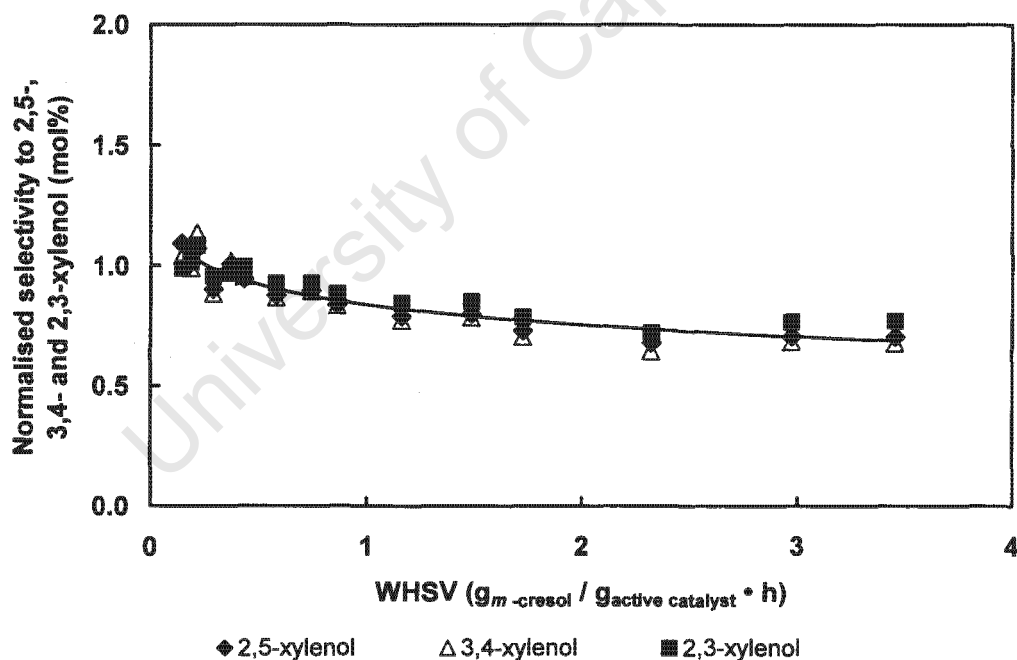


Figure 6-9b: Selectivity to individual primary xylene isomers, 2,5-, 3,4- and 2,3-xylene for variation in $\text{WHSV}_{m\text{-cresol}}$, normalised to the parameters of the trend lines shown in figure 6-9a

In figure 6-9b, selectivities are normalised to the averaged parameters of the logarithmic trend lines in figure 6-9a. Obviously there is no noticeable difference in trends. Correspondingly, ratios of primarily formed isomers as a function of conversion (figures 6-10 to 6-12 and 6-14 to 6-16) are constant. Selectivities to the other three isomers are

minor and only rise by a few percent at high conversion ($> 50\%$). The fact that the normalised curves of selectivity to 2,3- and 2,5-xylenol, at low $WHSV_{m\text{-cresol}}$ and high conversion, respectively, do not differ noticeably from the normalised curve of selectivity of 3,4-xylenol indicates towards minor contribution of intra-molecular 3-methylanisole transformation to xylenols, since enhanced *ortho*-selectivity, that would result from this reaction (see section 2.8.5), i.e. increased selectivity to 2,3- and 2,5-xylenol at high conversion (low $WHSV_{m\text{-cresol}}$), is not observed.

This means, on the other hand, that most of the 3-methylanisole that is consumed rapidly with increasing conversion, see figure 5-98, is converted to higher anisoles (that comprise most of the "others", see figure 5-100).

The 2,5- : 2,3-, 2,5- : 3,4- and 3,4- : 2,3-xylenol isomer ratios 300°C are close to 1 (see figures 6-17 to 6-19), so the reactivities of the '2', '4', and '6' positions in *m*-cresol are almost equal, also indicating that only very minor steric hindrance occurs between the adjacent methyl substituents.

At these conditions, low temperature and conversion, isomerisation between the isomers is minor.

Figures 6-14 to 6-16 represent various xylene isomer ratios at different conversions that were achieved through effective variation of $WHSV_{m\text{-cresol}}$ between 0.19 and 2.97 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$ in context of experiments varying feed ratio. It is concluded that a variation in $WHSV_{m\text{-cresol}}$ did not have any significant effect on the ratios of 2,5- : 2,3-xylenol, 2,5- : 3,4-xylenol or 3,4- : 2,3-xylenol, i.e. relative selectivities of the primary xylene isomers.

6.4.1.1 Order of reaction

Reaction orders were calculated using the methods detailed in appendix 5, the results of which are contained in section 5.5.5 (see figures 5-104 to 5-106). It was difficult to determine the reaction order via observation of the relevant figures. Plots for possible zero, first and second order reactions are shown in figures 5-104, 5-105 and 5-106, respectively. Linear regressions indicate that for $1 / WHSV_{m\text{-cresol}} < 3 \text{ g}_{\text{active catalyst}} \cdot \text{h} / \text{g}_{m\text{-cresol}}$ the overall reaction is of first order rather than second order.

It is likely that the reaction is first order, with respect to methanol, as the concentration of *m*-cresol within the catalyst pore system is high and phenol is present in huge surplus compared with methanol. It is therefore not likely to vary and can be assumed constant. The rate of the reaction is therefore only dependent on the concentration of adsorbed methanol on the active sites. Indeed it is reported that methanol is 1 000 000 times more

basic than phenol, so methanol will be the preferred adsorbed species given active Brønsted acid adsorption sites (Sykes, 1986).

Marczewski *et al.* (1996) reported that, in gas phase phenol alkylation with methanol at 200°C, the reaction was first order with respect to methanol but zero order with respect to phenol. This was accounted to the “capillary condensation” of phenol in the zeolite pores, i.e. the pores are almost completely filled with phenol, resulting in a constant concentration and high surplus of phenol in the vicinity of the acid sites, irrespective of the phenol concentration in the gas phase. Correspondingly this also holds for high pressure and in liquid phase. Thus it seems likely that a similar phenomenon is occurring in the methylation of *m*-cresol with methanol over zeolites. According to conclusions made by Moon *et al.* (2004) in the alkylation of phenol with methanol over zeolite H-MCM-22, the enhancement in *p*-selectivity that was observed at high reaction pressure (around 30 bar) was ascribed to enhanced diffusion constrictions due to the almost complete occupation of the zeolite pore system with phenol.

It is assumed that, the reaction proceeds via a Rideal mechanism with methanol being adsorbed and *m*-cresol reacting from the fluid phase (see section 2.8.9).

6.4.2 Pressure effect

In order to gauge the effect of pressure, two series of experiments were carried out, one at 300°C, 0.09 g_{*m*-cresol} / g_{active catalyst} · h and one at 350°C, 3.72 g_{*m*-cresol} / g_{active catalyst} · h within which the operating pressure was varied. In the first series, pressure was increased from 40 bar to 80 bar. In the second, pressure was decreased from 80 bar to 30 bar.

In both series the results show that conversion increased with increasing operating pressure (figures 6-10 to 6-12 and figure 5-74). So does the yield of xylenols (figure 5-76).

It is likely that this is mainly due to higher concentration of gas phase methanol being dissolved in the liquid *m*-cresol phase at higher pressure and the higher surface concentration of adsorbed methanol on the catalyst (see section 6.4.4.1).

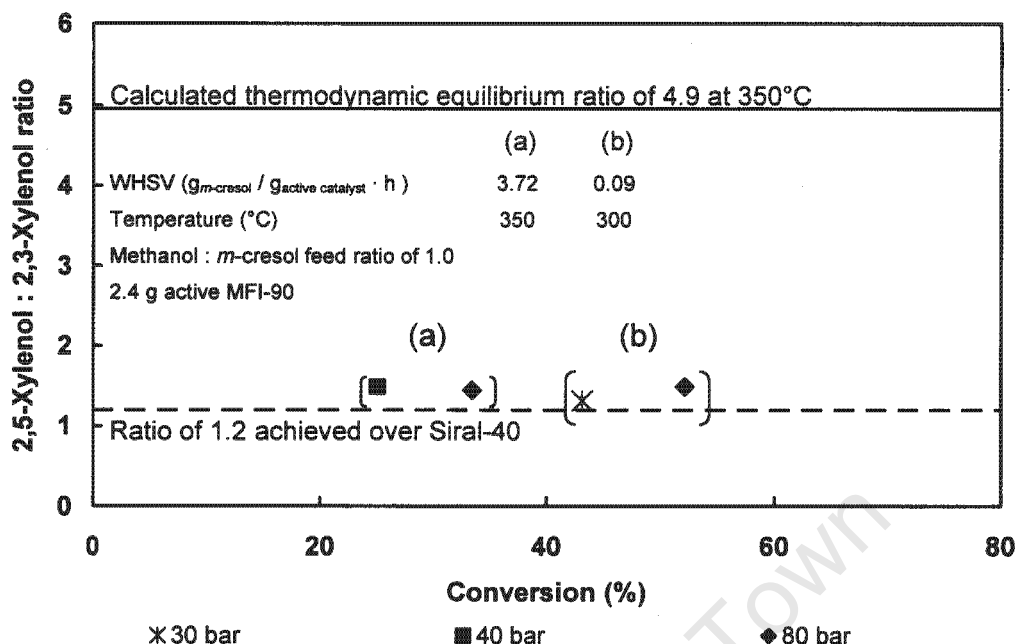


Figure 6-10: 2,5- : 2,3-Xylenol ratios for different pressures as a function of *m*-cresol conversion (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

Product distribution varies with total pressure, in the same way as in $\text{WHSV}_{m\text{-cresol}}$ studies i.e. only depending on conversion (compare figures 5-75 and 5-77 to 5-83 with figures 5-95 and 5-98 to 5-103, respectively). This aspect is addressed again and discussed in detail in section 6.4.5.

Xylenol isomer ratios, a comparably sensitive measure (see introduction to section 6.2), which are still kinetically controlled and not influenced by pressure, see figures 6-10 to 6-12. This also applies to the 3,4- : 2,3-xylenol ratio shown in figure 6-12.

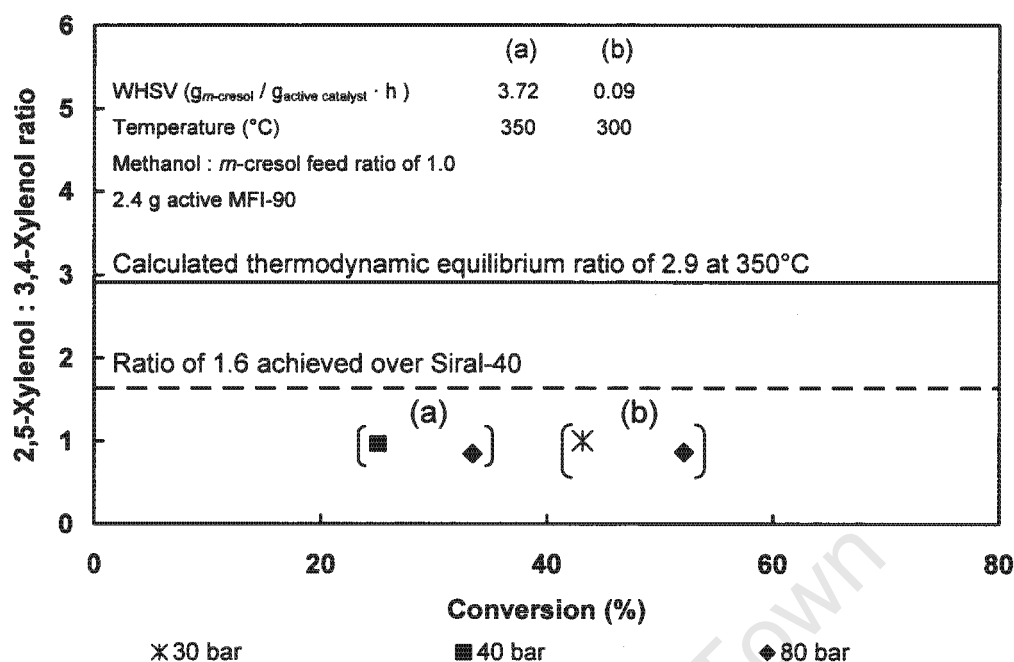


Figure 6-11: 2,5- : 3,4-Xylenol ratios for different pressures as a function of conversion (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

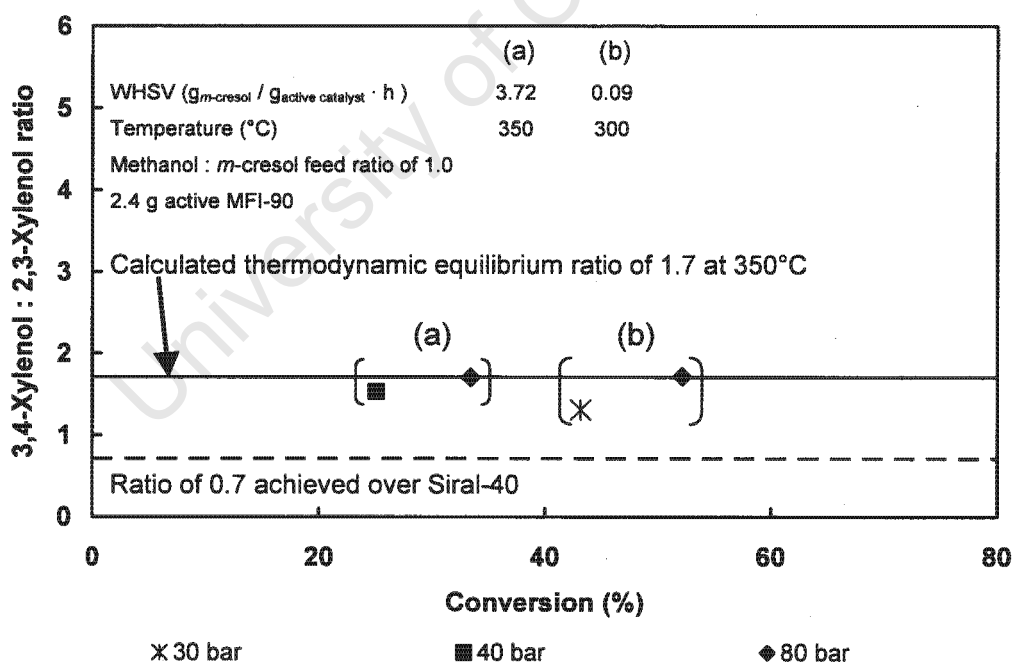


Figure 6-12: 3,4- : 2,3-Xylenol ratios for different pressures as a function of conversion (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999)

6.4.3 Methanol : *m*-cresol ratio effect

6.4.3.1 Methanol availability

It has been reported that over H-ZSM-5 methanol consumption in parallel reactions began limiting the overall conversion of phenols, since most of the methanol was consumed in side reactions, particularly during the initial stages of the reaction (Balsama *et al.*, 1984). Such an effect was not observed in any of these experiments, although not specifically investigated, as only the liquid product was collected and analysed. However, in most cases *m*-cresol conversion under base case conditions was at around 40 to 60 %, just achieving 71 % in run CM D6 over BEA-150 (see table 5-4). Even at the low molar methanol : *m*-cresol feed ratio of 0.5 a reasonable amount of *multi*-alkylated products was formed.

6.4.3.2 Methanol : *m*-cresol ratio variation

For each feed ratio employed the $WHSV_{m-cresol}$ varied (see appendix 6). Thus conversions were linearly normalized to the $WHSV_{m-cresol}$ of the experiment with the molar feed ratio of 1.0, so that each group of data points refers to equal $WHSV_{m-cresol}$ and only shows the ratio effect. Figure 6-13 shows the normalised conversions obtained for different methanol : *m*-cresol ratios over MFI-90 at 300°C. The original data (i.e. prior to normalisation) can be found in figure 5-84.

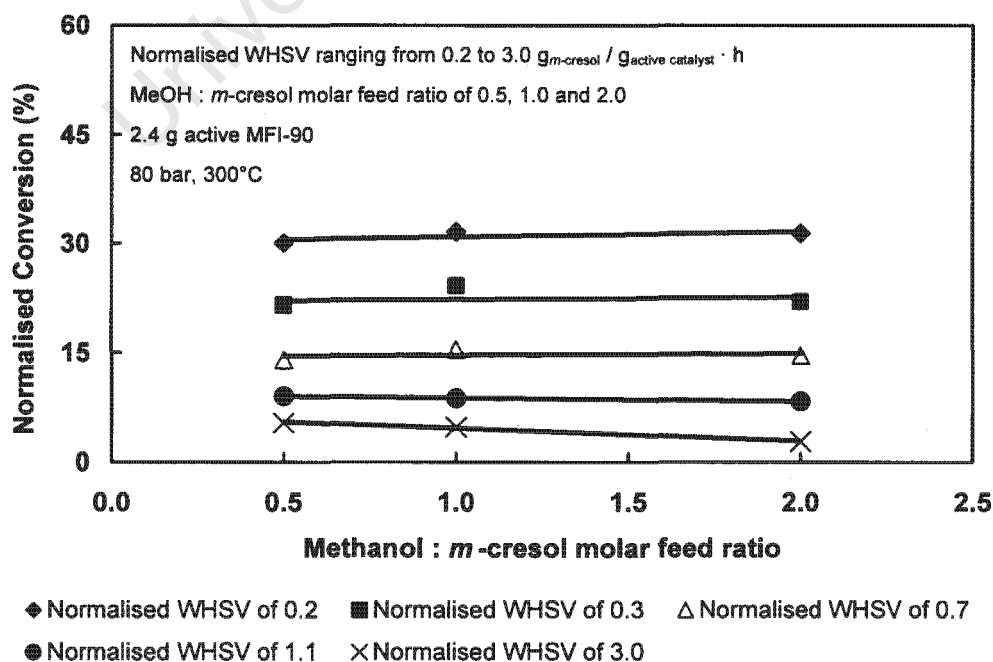


Figure 6-13: Normalised conversion of *m*-cresol versus methanol : *m*-cresol molar feed ratio for *m*-cresol methylation over MFI-90 at different normalised space velocities. The original data points can be found in figure 5-84.

As illustrated in figures 6-14 to 6-16 and figures 6-17 to 6-19 the feed ratio had some, but very little effect on conversion with conversion being the highest at a ratio of 1.0 but this order is somewhat flawed by, or even due to experimental scatter. However, this effect is minor, if existing at all.

Experimental trends suggest that the selectivity to total xylenol product was unaffected by the molar methanol : *m*-cresol feed ratio (figure 5-85). There was also no variation either in terms of individual xylenol isomers (see figures 5-91 to 5-93) or any other products (figures 5-88 to 5-90), at least over the range of feed ratios, 0.5 to 2.0, covered in the experiments. Very subtle differences or trends may be masked by data scatter, since expectations suggest towards an increase in degree of methylation with increasing methanol : *m*-cresol feed ratio (see sections 2.8.10.1 and 2.10.5). Trivially, the ratios of selectivities of the three major xylenol isomers, figures 6-14 to 6-16, were also not affected at all by variation in the feed ratio.

The position of the *m*-cresol substrate, where and to which extent 'C' and 'O' alkylation takes place, is controlled by the chemical properties of the *m*-cresol molecule, not by the abundance of alkylating agent.

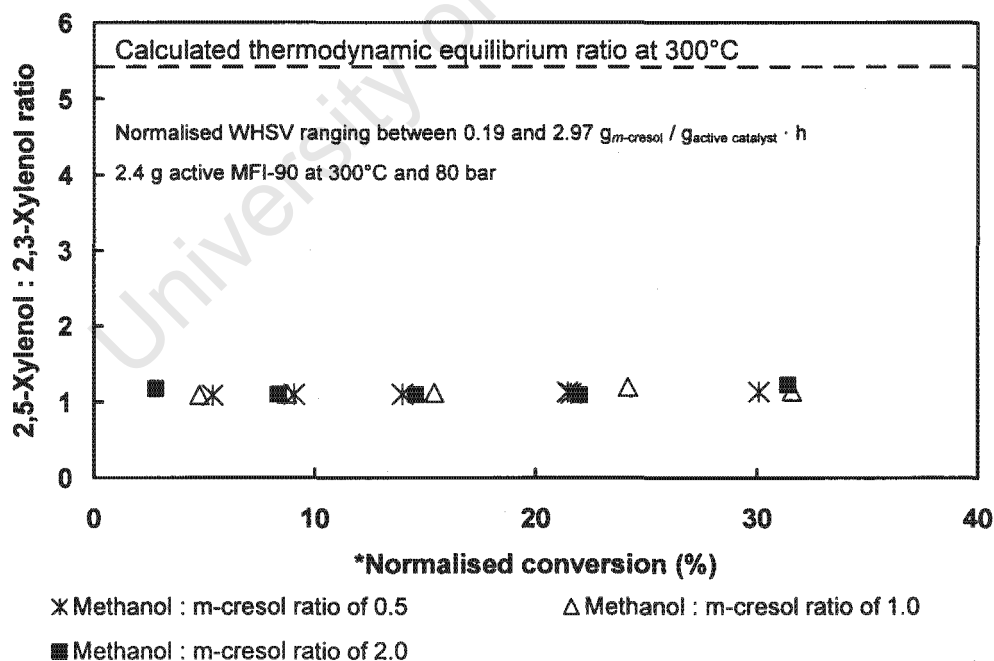


Figure 6-14: 2,5- : 2,3-Xylenol ratios as a function of normalised conversion for different methanol : *m*-cresol feed ratio (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). *See main text.

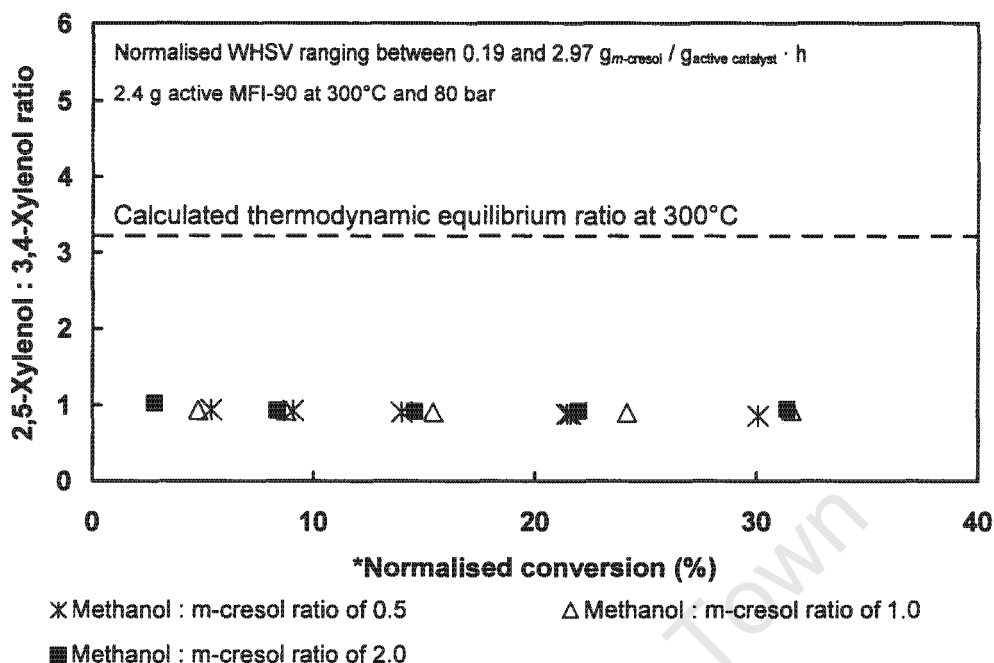


Figure 6-15: 2,5- : 3,4-Xylenol ratios as a function of normalised conversion for different methanol : *m*-cresol feed ratio (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). *See main text.

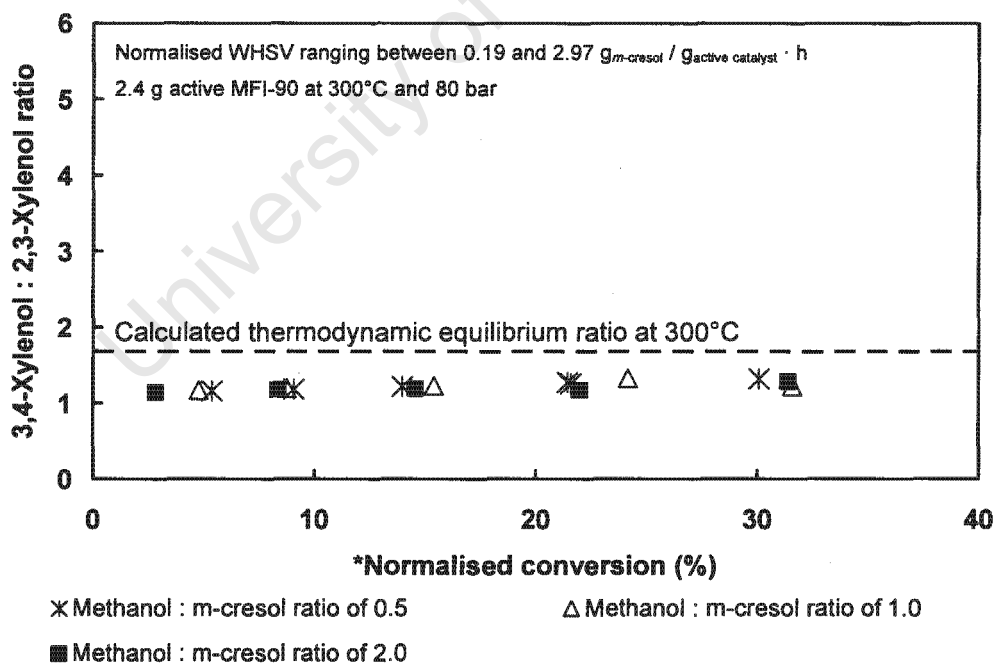


Figure 6-16: 3,4- : 2,3-Xylenol ratios as a function of normalised conversion for different methanol : *m*-cresol feed ratio (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). *See main text.

6.4.4 Temperature effect

The effect of temperature on the product distribution was very briefly investigated over only one of the catalysts tested, MFI-90. Conversion more than doubled from around 20 % to around 50 % when temperature was increased from 300 to 350°C (see figure 5-60 and figures 6-17 to 6-19).

Yield of xylenols increased correspondingly with increasing temperature (figure 5-62), however, the percentage of xylenols within the phenolic product declined (figure 5-63) due to the formation of trimethylphenols (see figure 5-65) and other higher alkylated products (figure 5-66) at those enhanced conditions. 3-Methylanisole almost vanished at 350°C (figure 5-64). The selectivities to the individual xylene isomers changed as well, see figures 5-67 to 5-72. Figures 6-17 to 6-19 have been drawn to illustrate the effect of temperature on selectivity, just driving xylene isomer ratios towards thermodynamic equilibrium, essentially at the cost of the thermodynamically very unstable 2,3-xylene isomer (see figure 5-69). Changes in 2,5- : 2,3- and 3,4- : 2,3-xylene ratios are by factor 2, approximately, while the 2,5- : 3,4-xylene ratio doesn't change much.

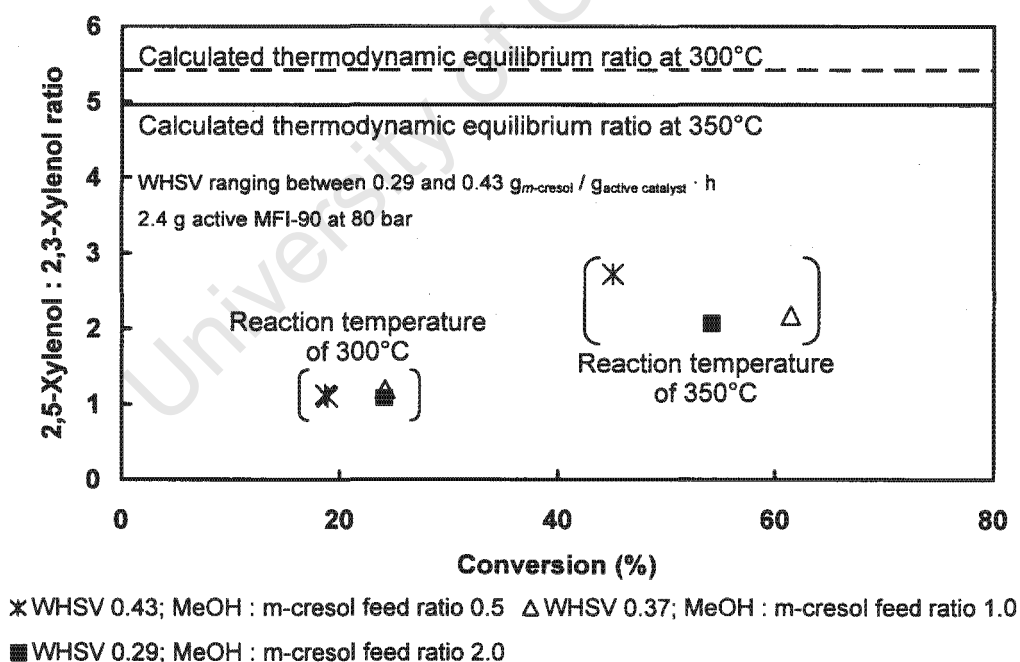
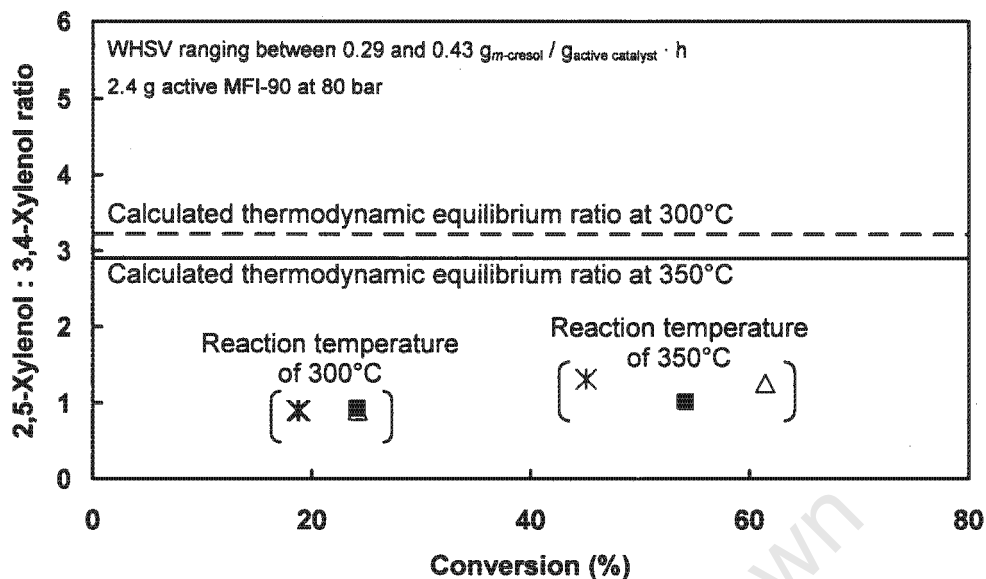


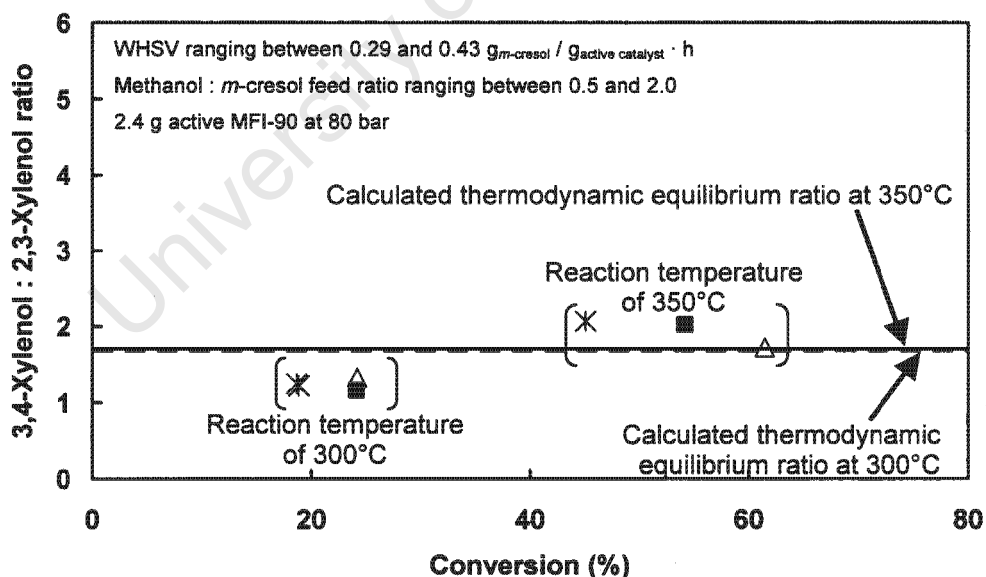
Figure 6-17: 2,5- : 2,3-xyleneol ratios as a function of conversion at different reaction temperatures (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). Note that the differences in $WHSV_{m-cresol}$ result from the different feed compositions, pumped at equal flow rates and thus equal $LHSV_{feed}$.



X WHSV 0.43; MeOH : m-cresol feed ratio 0.5 △ WHSV 0.37; MeOH : m-cresol feed ratio 1.0

■ WHSV 0.29; MeOH : m-cresol feed ratio 2.0

Figure 6-18: 2,5- : 3,4-xylenol ratios as a function of conversion at different reaction temperatures (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). Note that the differences in $\text{WHSV}_{m\text{-cresol}}$ result from the different feed compositions, pumped at equal flow rates and thus equal $\text{LHSV}_{\text{feed}}$.



X WHSV 0.43; MeOH : m-cresol feed ratio 0.5 △ WHSV 0.37; MeOH : m-cresol feed ratio 1.0

■ WHSV 0.29; MeOH : m-cresol feed ratio 2.0

Figure 6-19: 3,4- : 2,3-xylenol ratios as a function of conversion at different reaction temperatures (calculations performed for ideal gas phase thermodynamic equilibrium mixture as in appendix 1, thermodynamic data from Daubert *et al.*, 1999). Note that the differences in $\text{WHSV}_{m\text{-cresol}}$ result from the different feed compositions, pumped at equal flow rates and thus equal $\text{LHSV}_{\text{feed}}$.

6.4.4.1 Activation energies

As discussed previously, the activation energy of the reaction can indicate whether the reaction experienced any diffusion limitations or thermodynamic constraints (see section 2.6.2). For methylation of *m*-cresol at 300°C and 350°C over H-MFI, the activation energy calculated for it as a first order reaction was 86 kJ / mol (table 5-6). The calculated activation energy was significantly higher than that of 50 – 67 kJ / mol, as calculated by Santacesaria *et al.* (1990b) for methylation of phenol with methanol over MFI for temperatures between 300°C and 331°C (table 2-13). Therefore, in the case of *m*-cresol methylation, the overall reaction probably experienced no mass transfer constraints.

The activation energy for each of the major phenolic products (2,5-xyleneol, 3,4-xyleneol, 2,3-xyleneol and total xyleneols) was also determined and found to be 72, 54 and 25 kJ / mol, respectively. The low activation energy (table 5-6) of 25 kJ / mol for 2,3-xyleneol may indicate towards some mass transfer effects on this rather bulky xyleneol isomer. However, it must be pointed out, that these calculated activation energies have been determined over a regime in which the conversion was reasonably high, so primarily produced 2,3-xyleneol may also have experienced some consumption in secondary reactions, as the data does suggest (see section 6.3.2).

Thus it makes little sense to draw too deep conclusions from the activation energies of the formation of major products as some of them are intermediates that were consumed in subsequent secondary reactions.

In addition, it is likely that the heat of adsorption of phenolic species or methanol onto the active sites of the acid zeolite is of similar magnitude as the calculated activation energy and could be contributing to some reduction of the apparent activation energy compared to the true activation energy (see equation 6-1).

Equation 6-1: Illustration of contribution of enthalpy of adsorption (ΔH_{ads}) to apparent activation energy (E_A)

$$r = k' \cdot C^n$$

$$r = k \cdot K \cdot C^n$$

$$r = k^0 \cdot e^{\frac{-E_A}{R \cdot T}} \cdot K^0 \cdot e^{\frac{-(-\Delta H_{ads})}{R \cdot T}} \cdot C^n$$

$$r = k^{0'} \cdot e^{\frac{-E_A - (-\Delta H_{ads})}{R \cdot T}} \cdot C^n$$

$$r = k^{0'} \cdot e^{\frac{-(E_A - \Delta H_{ads})}{R \cdot T}} \cdot C^n$$

6.4.5 Comparison between the effects of WHSV, feed ratio, pressure and temperature on selectivity

A comparison between the effects of WHSV and conversion on selectivity to products on the one hand and feed ratio, pressure and temperature on the other can indicate whether the observed differences due to these variations are true effects or merely secondary effects via conversion. Figures 6-20 to 6-26 portray selectivity to various products versus conversion for two sets of experiments: variation of $\text{WHSV}_{m\text{-cresol}}$, methanol : *m*-cresol molar feed ratio, pressure and temperature.

For selectivity to total xylenol product (figure 6-20) it is clear that the data obtained at 300°C follows the same trend regardless of which reaction parameter ($\text{WHSV}_{m\text{-cresol}}$, feed ratio, pressure) was varied. Thus it is likely that the variation of these parameters did not directly affect selectivity to total xylenol product, but that the effect was secondary in nature, i.e. just via change of conversion. However, the trend caused by variation in temperature differs, indicating towards a direct effect of temperature on selectivity.

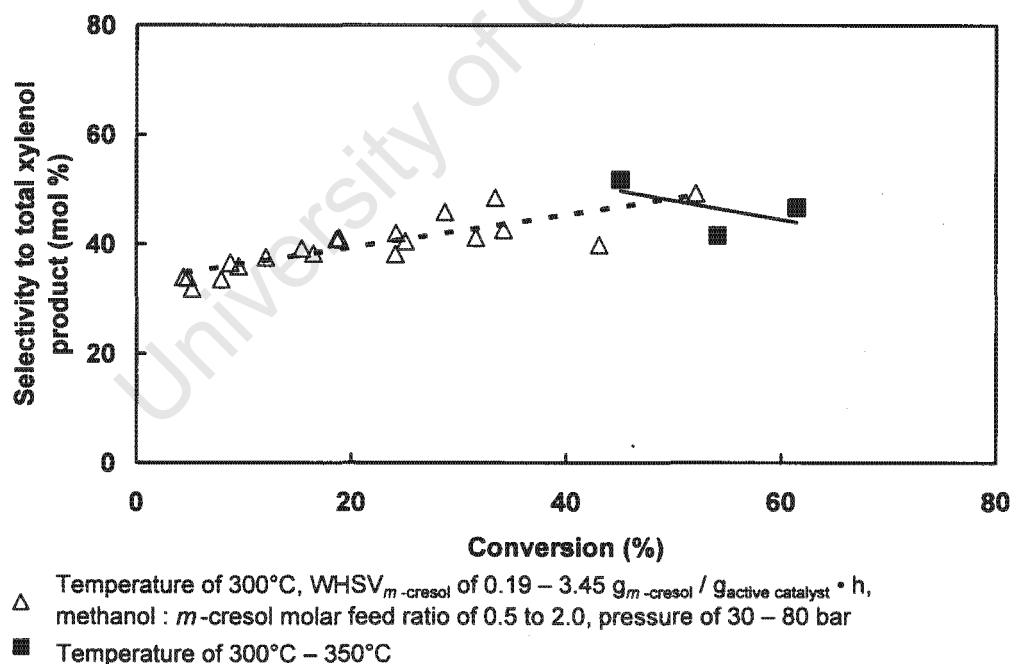


Figure 6-20: Selectivity to total xylenol product at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of WHSV, feed ratio, temperature and pressure on selectivity.

Figures 6-21, shows a similar level and trend of selectivity to 3-methylanisole for variation in $\text{WHSV}_{m\text{-cresol}}$, methanol : *m*-cresol molar feed ratio and pressure. However, the trend caused by variation in temperature differs.

Similar trends for the effects of $WHSV_{m\text{-cresol}}$, methanol : *m*-cresol molar feed ratio and pressure but a somewhat deviating trend for the temperature effect are seen for selectivity to trimethylphenols (figure 6-22) and to "others" (figure 6-23).

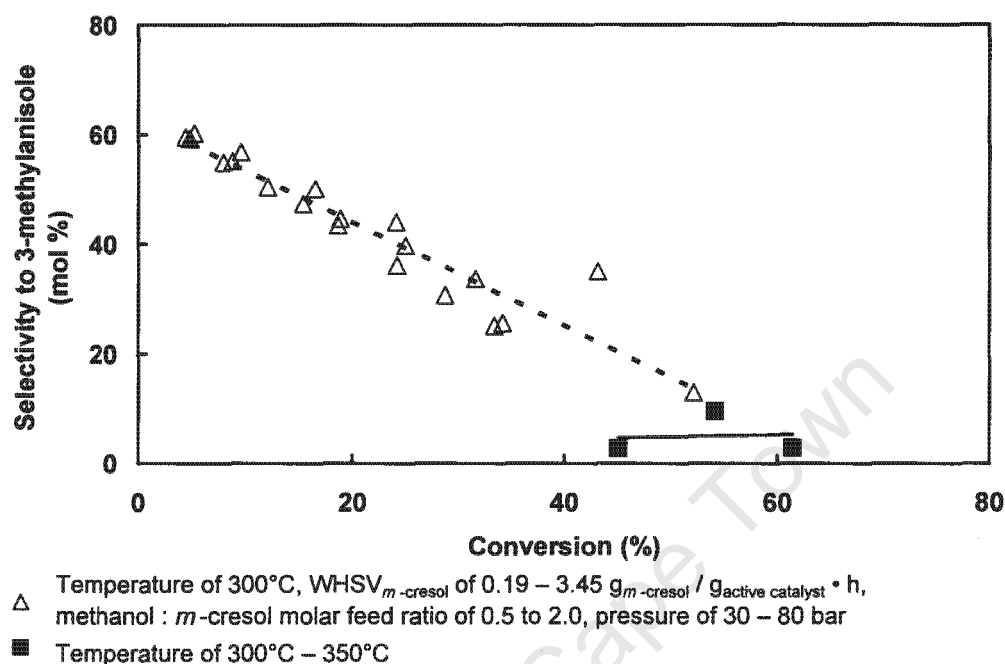


Figure 6-21: Selectivity to 3-methylanisole at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of $WHSV$, feed ratio, temperature and pressure on selectivity.

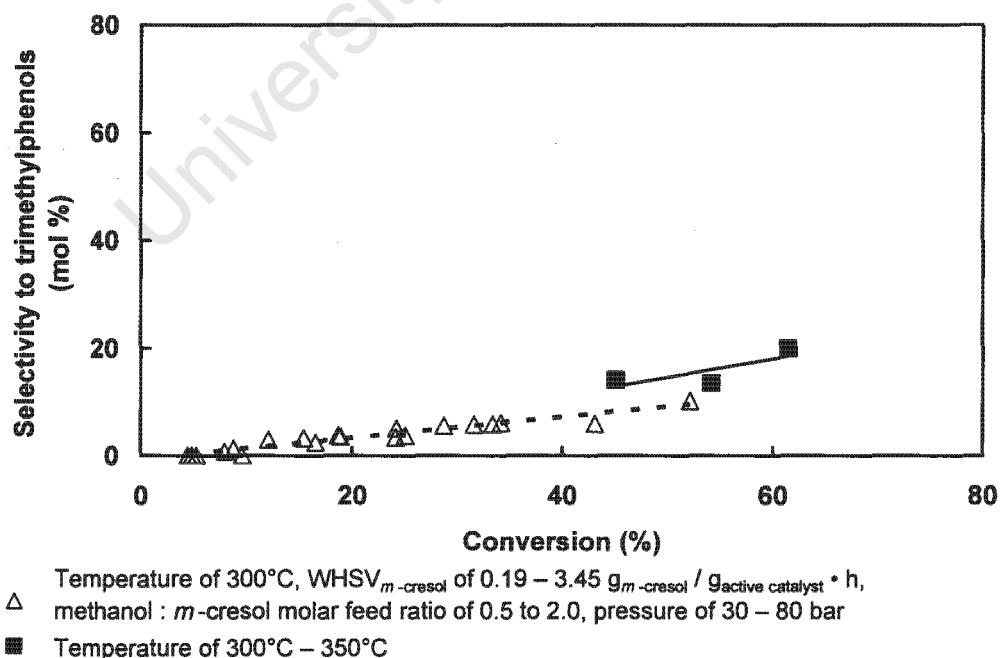


Figure 6-22: Selectivity to trimethylphenol isomers at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of $WHSV$, feed ratio, temperature and pressure on selectivity.

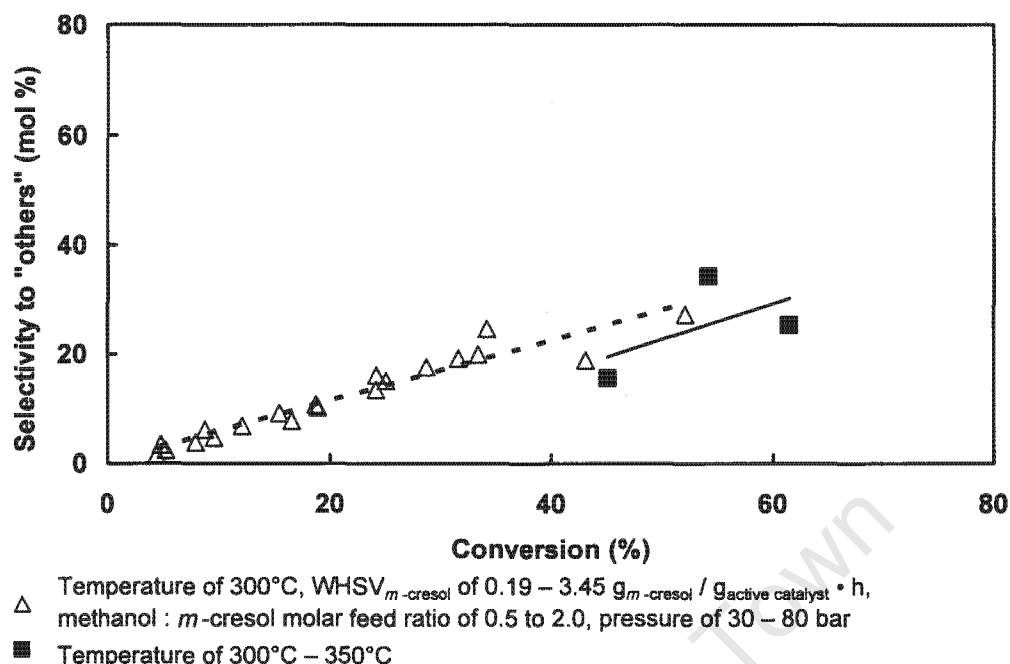


Figure 6-23: Selectivity to "others" at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of WHSV, feed ratio, temperature and pressure on selectivity.

Selectivity to 2,5-xylenol indicates a separate temperature effect on selectivity (figure 6-31) but no direct effect of $WHSV_{m-cresol}$, methanol : *m*-cresol molar feed ratio or pressure.

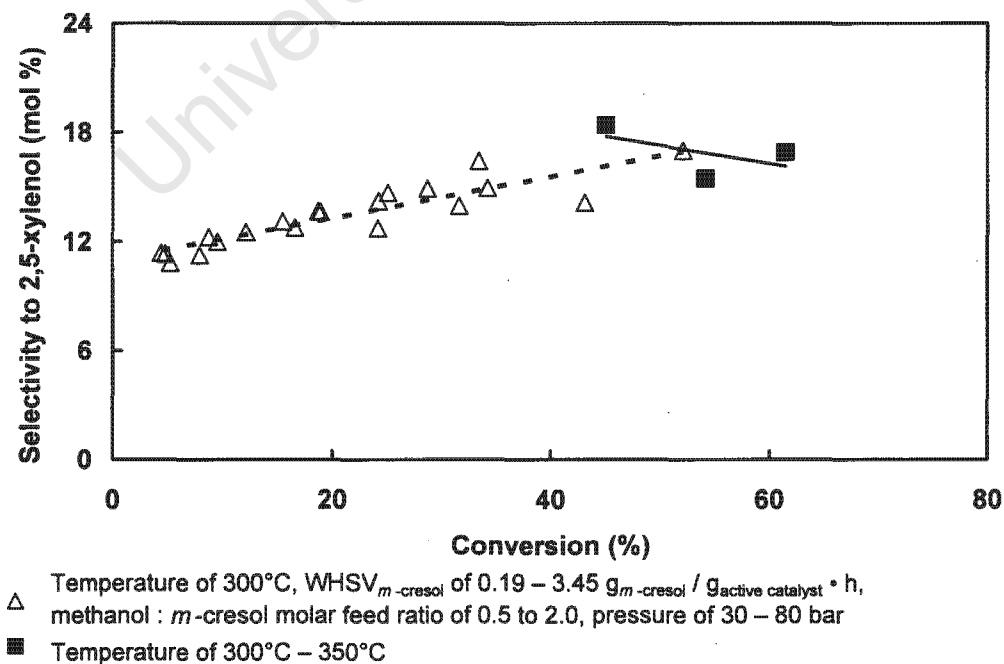


Figure 6-24: Selectivity to 2,5-xylenol at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of WHSV, feed ratio, temperature and pressure on selectivity.

Selectivities to 3,4-xylenol and 2,3-xylenol indicate evidence of a temperature effect as well (figures 6-25 and 6-26) while effects of $\text{WHSV}_{m\text{-cresol}}$, methanol : *m*-cresol molar feed ratio and pressure, again only influence indirectly, via conversion.

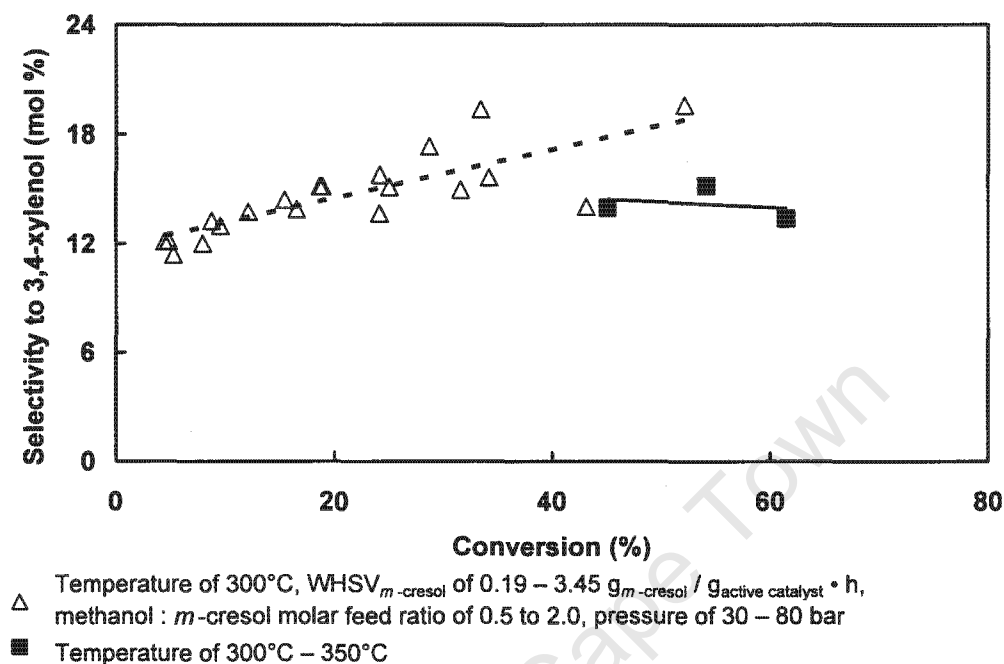


Figure 6-25: Selectivity to 3,4-xylenol at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of WHSV, feed ratio, temperature and pressure on selectivity.

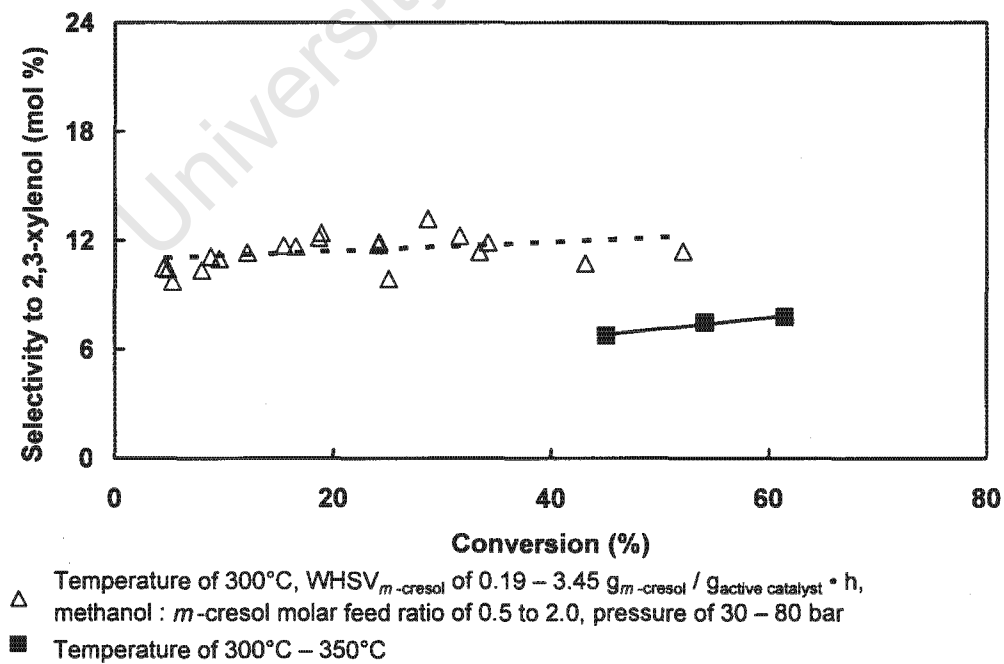


Figure 6-26: Selectivity to 2,3-xylenol at different conversions. The data here are from different experiments in which *m*-cresol was methylated with methanol over MFI-90 for comparison between the effects of WHSV, feed ratio, temperature and pressure on selectivity.

6.4.6 Crystal surface effects

The proportion of product being produced on the external surface of the crystals was not investigated. While there probably were plenty active sites on the external surface of the small zeolite crystals applied, it is possible that a significant amount of product was produced in external surface reactions. This would affect the extent of shape selectivity of the zeolites, however, since there wasn't any, except apparently a little over MOR-90 and FER-20, this didn't play a role. On the other hand, most of the initial decline of activity that was observed over the fresh zeolite samples (see figures 5-2 and 5-3 and section 6.1.7) can be ascribed to coking and deactivation of the external surface sites. Since comparison of zeolites and effects of reaction conditions was only performed using steady state or quasi-steady state product samples, the phenomenon of product from external sites flawing the results can essentially be excluded.

6.5 Summary of major aspects of the discussion

- The mechanism indicates that the primary reaction proceeds along two parallel paths, 'O' alkylation and 'C' alkylation. Under the reaction conditions applied (300°C), 'O' alkylation is dominant over 'C' alkylation in a ratio of approximately 3 : 2
- With increasing conversion the majority of 3-methylanisole is alkylated further while only some of it undergoes an intra-molecular rearrangement, forming xlenols
- Compared to thermodynamic equilibrium distribution, much higher proportions of 2,5-, 3,4- and 2,3-xlenol are formed within the xlenol fraction
- The above are the kinetically preferred primary ring alkylation products
- Selectivity to and yield of 3-methylanisole decreases at high conversion due to increasing consumption in secondary reactions, while yield of phenolic compounds still increases and selectivity stays almost constant
- Significant secondary reactions of the primarily formed xlenol isomers do not take place
- The effect of reaction conditions, $WHSV_{m-cresol}$, methanol : *m*-cresol molar feed ratio and pressure on selectivity, is indirect, only via their influence on conversion
- There is, however, a direct effect of temperature on selectivity, which is independent of its effect on conversion
- Conversion increases significantly with lower $WHSV$ and higher temperature and somewhat with increasing pressure

- The feed ratio has practically no effect on conversion
- Significant differences have been observed between the activities of the catalysts tested
- Differences in selectivity between the catalysts tested are not very pronounced
- However, medium pore zeolite FER-20 as well as zeolite MOR-90, with its monodimensional pore system, favour the most linear isomer, 2,5-xyleneol, i.e. are somewhat shape selective, but the observed effect is weak
- In the trimethylphenol fraction, MFI zeolites significantly favour the 2,4,5-isomer, which is the slimmest isomer of the trimethylphenol isomers
- BEA-150 is more porous, compared with the other zeolites tested, due to the 3-dimensional pore system and larger pore size (6.6 x 6.7 Å). Thus zeolite BEA-150 produced more higher alkylated product molecules
- Large pore zeolites, BEA-150 and MTW-100 and amorphous Siral-40 favour the most bulky isomers 2,3-xyleneol and 2,3,6-trimethylphenol
- Higher temperature accelerates 1,2-shift isomerisation, driving the xyleneol isomers distribution in the direction of thermodynamic equilibrium
- Apparently, the overall reaction is of first order with respect to methanol and zero order with respect to *m*-cresol, indicating towards a Rideal mechanism, with methanol being adsorbed and *m*-cresol reacting from the fluid phase
- Apparent activation energy for the overall reaction was determined to be around 86 kJ / mol, indicating towards a non-mass transfer controlled reaction.

7. Conclusions

The following conclusions can be drawn:

- Acid zeolite based catalysts are active and, after an initial stabilisation period, are stable for the methylation reaction of *m*-cresol with methanol.
- The usual makes of industrial zeolite based catalysts are not suitable to effect product shape-selective methylation of *m*-cresol with methanol. This is mainly because the size of the zeolite crystals is too small. Zeolite crystals in such catalysts usually have diameters of only 0.1 – 0.2 μm .
- However, zeolites FER and MOR showed a weak product shape-selective effect, slightly favouring the slimmest xylene isomer, 2,5-xylene.
- Nevertheless, there is evidence that over some of the materials used (essentially the MFI based catalysts) the more bulky trimethylphenol isomers experienced some diffusion constraints, i.e. product shape-selectivity is influencing product distribution.
- Over the range of conditions varied, no enhancement of the observed shape-selective effects, which are weak anyway, could be achieved with high selectivities.

8. Recommendations

Future research on this subject should focus on the following:

- In order to get more pronounced product shape-selective effects, larger zeolite crystals of the FER, MFI and MOR type should be applied, due to the particle size effect on the Thiele Modulus.
- Lengths of diffusion pathways should be increased by other methods as well (e.g. blocking of parts of the internal pore systems by impregnation e.g. with salts or blocking most of the pore mouths e.g. by chemical vapour or liquid deposition of silica or pre-coking).
- Effect of lowermost silica-alumina ratios should be investigated due to its effect on the Thiele Modulus via the reaction rate constant.
- Deactivating the external crystal surface should improve shape selectivity and preserve the formation of a possible shape-selective product inside the crystals.
- The reaction should be conducted at low conversion (i.e. rather high space velocity) to prevent the loss of xlenols in secondary reactions.
- The reaction should be conducted at sufficiently high temperature, $\geq 350^{\circ}\text{C}$, to prevent 3-methylanisole and higher anisoles being formed.

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Appendix 1: Thermodynamic Calculations

1. Thermodynamic data

Thermodynamic data were taken from Daubert *et al.* (1999) and Perry (1997).

Data from Daubert *et al.*, (1999) were used to calculate thermodynamic equilibria for the alkylation of *m*-cresol with methanol to xlenol isomers and the equilibrium ratios of the xlenol isomers.

Data from Perry (1997) were used to calculate the equilibrium for the condensation reaction of two moles of methanol to dimethylether and water.

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2. Converting Calculated Heat Capacity into a Quadratic Function

Daubert *et al.* (1999) have published data that can be used to calculate the heat capacities of various compounds. The equation to be used is depicted in equation A1-1.

Equation A1-1: The equation used in determining heat capacity at a specific temperature (T) according to Daubert *et al.* (1999). The constants A, B, C, D and E are listed in thermodynamic data tables as published by Daubert *et al.* (1999), see example in table A1-1

$$C_p(T) = A + B \cdot \left[\frac{\left(\frac{C}{T} \right)}{\sinh\left(\frac{C}{T}\right)} \right]^2 + D \cdot \left[\frac{\left(\frac{E}{T} \right)}{\cosh\left(\frac{E}{T}\right)} \right]^2$$

However, this equation requires excessive computing in order to determine the heat of reaction at a specific temperature $\Delta H_{rxn}(T)$.

Thus heat capacities were plotted for 50 temperature values in 25°C steps over the range for which data are supplied by Daubert *et al.* (1999). Then a quadratic function was trended over the calculated heat capacities, see figure A1-1 (method adapted from van Steen, 2003).

The following example illustrates the calculation of heat capacities depending on temperature (in quadratic format) for *m*-cresol. See table A1-1 and equation A1-2.

Table A1-1: Constants used in calculating the heat capacity of *m*-cresol using equation A1-1 for temperature range of -73°C to 1227°C for which data are published by Daubert *et al.* (1999)

A	B	C	D	E	Range (°C)	
					Minimum	Maximum
$4.34 \cdot 10^4$	$2.45 \cdot 10^5$	$1.15 \cdot 10^3$	$1.51 \cdot 10^5$	$-5.07 \cdot 10^2$	-73	1227

Equation A1-2: An example showing the constants A, B, C, D and E, as from table A1-1 inputted into equation A1-1 to determine the heat capacity of *m*-cresol at 350°C (623K)

$$C_p(623K) = 4.34 \cdot 10^4 + 2.44 \cdot 10^5 \cdot \left[\frac{\left(\frac{1.15 \cdot 10^3}{623} \right)}{\sinh\left(\frac{1.15 \cdot 10^3}{623}\right)} \right]^2 + 1.51 \cdot 10^5 \cdot \left[\frac{\left(\frac{-5.07 \cdot 10^2}{623} \right)}{\cosh\left(\frac{-5.07 \cdot 10^2}{623}\right)} \right]^2$$

$$C_p(623K) = 185 \text{ J / mol} \cdot \text{K}$$

Figure A1-1 shows the calculated heat capacities of *m*-cresol plotted against temperature at 25°C intervals between -73°C and 1227°C and the quadratic trend line (equation A1-3).

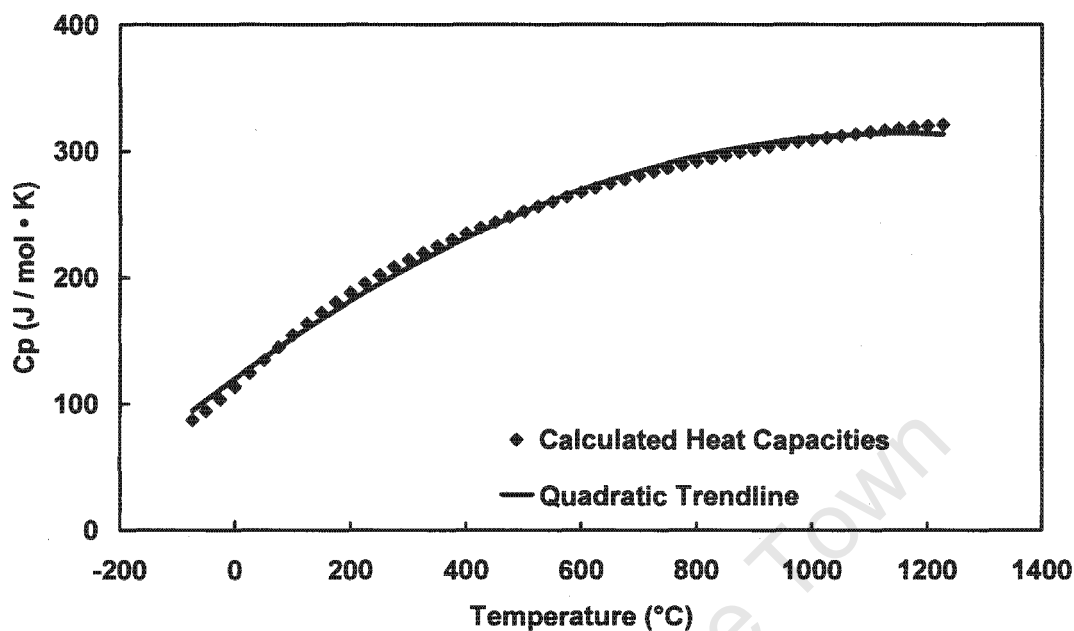


Figure A1-1: Calculated heat capacities of *m*-cresol and quadratic trend line (thermodynamic data used in calculating heat capacities from Daubert *et al.*, 1999)

In all cases the R-squared values were greater than 0.99.

Equation A1-3: The format of the quadratic equation used to trend calculated heat capacities

$$C_p(T) = a + b \cdot T + c \cdot T^2$$

The constants, *a*, *b* and *c*, determined for various compounds, are shown in tables A1-2.

Appendix 1: Thermodynamic Calculations

Table A1-2: Constants for the quadratic equation (equation A1-3) to calculate heat capacities of the major compounds in the reaction mixture from *m*-cresol methylation

	Constants		
	a	b	c
	$J/mol \cdot K$	$J/mol \cdot K^2$	$J/mol \cdot K^3$
<i>o</i>-Cresol	26.8	0.398	-0.000138
<i>m</i>-Cresol	23.5	0.404	-0.000141
<i>p</i>-Cresol	23.2	0.404	-0.000141
Anisole	4.8	0.426	-0.000147
Methanol	17.3	0.099	-0.000027
Water	30.6	0.009	0.000002
2,3-Xylenol	48.5	0.453	-0.000155
2,4-Xylenol	36.9	0.470	-0.000161
2,5-Xylenol	38.4	0.467	-0.000160
2,6-Xylenol	36.9	0.467	-0.000159
3,4-Xylenol	47.3	0.457	-0.000155
3,5-Xylenol	31.1	0.479	-0.000165

3. Calculating Thermodynamic Equilibria of Reaction

Calculating thermodynamic equilibria for alkylation of *m*-cresol with methanol to xlenol isomers and water

The inherent physical and chemical properties of individual compounds determine the behaviour of that compound when undergoing a reaction. In addition, the local conditions (e.g. temperature and pressure) influence reaction pathways and affect the extent to which the reaction proceeds.

In general, each and every reaction attempts to proceed towards a point where equilibrium is achieved. In many cases the rate of reaction is slow and equilibrium is only achieved after long periods of time. If the equilibrium of a particular reaction is known, then the actual progress of the reaction can be measured against approach to the equilibrium.

This section outlines how the equilibrium conversions of the major reactions in the reaction mixture of *m*-cresol methylation are calculated. Equations hold for ideal gas state reactions. The reaction between *m*-cresol and methanol, forming 2,5-xlenol and water is used as an example (refer to equation A1-4).

Equation A1-4: Conversion of *m*-cresol and methanol to 2,5-xlenol and water



In order to calculate the equilibrium for the above reaction in liquid phase the activity coefficients of each of the compounds must be known. The activity coefficient of the phenolic compounds (*m*-cresol and 2,5-xlenol) can be assumed similar and close to unity. However, the activity coefficients of methanol and water will differ. As these activities are not known, it is not possible to conduct equilibrium calculations for the liquid phase reaction.

By assuming ideal gas behaviour for the reaction system, where all fugacity coefficients are equal to unity, it is possible to carry out equilibrium conversion calculations. Equation A1-5 shows the relationship between Gibbs free energy of reaction and equilibrium constant K_{eq} , where T is the reaction temperature (K), P is the reaction pressure and R is the ideal gas constant (8.314 J / mol · K) (Sandler, 1989).

Appendix 1: Thermodynamic Calculations

Equation A1-5: Equilibrium constant K_{eq} between the reactants and products for an ideal gas phase reaction (Sandler, 1989)

$$\prod_i x_i^{v_i} = e^{\left[-\frac{\sum_i v_i G_{f,i(mol)}(T,P)}{RT} \right]} = K_{eq}$$

The reaction between *m*-cresol and methanol is an equimolar reaction, consuming one mole each of *m*-cresol and methanol and forming one mole of each 2,5-xyleneol and water. Table A1-3 illustrates the change in moles.

Table A1-3: Change in moles of reactants and products in the reaction of *m*-cresol with methanol to 2,5-xyleneol and water

Compound	Moles in	Change in moles	Moles out	Mole fraction out
<i>m</i> -Cresol	1	-X	(1-X)	(1-X)/2
Methanol	1	-X	(1-X)	(1-X)/2
2,5-Xyleneol	-	X	X	X/2
Water	-	X	X	X/2
Total moles	2	-	2	-

Using the final mole fractions in table A1-3, the ideal gas phase equilibrium constant, K_{eq} , can be equated to the equilibrium concentration of reactants and products. This can thus be used to determine the equilibrium conversion, X_{eq} . Thus it is possible to transform equation A1-5 by relating the Gibbs free energy of reaction to the ideal gas phase equilibrium concentration. This relationship is shown in equation A1-6.

Equation A1-6: Ideal gas phase equilibrium constant K_{eq} and the relationship with the change in Gibbs free energy (which equals Gibbs free energy of reaction, $-\Delta G_{rxn}(T)$) at reaction temperature T for equation A1-4 (based on Sandler, 1989)

$$K_{eq} = \frac{\left(\frac{X_{eq}}{2}\right) \cdot \left(\frac{X_{eq}}{2}\right)}{\left(\frac{1-X_{eq}}{2}\right) \cdot \left(\frac{1-X_{eq}}{2}\right)} = \left(\frac{X_{eq}}{1-X_{eq}}\right)^2 = e^{\frac{-\Delta G_{rxn}}{RT}}$$

This reaction is equimolar, therefore, no pressure term appears and the reaction pressure does not influence the equilibrium.

Equation A1-6 can be further reduced to equation A1-7.

Equation A1-7: Relationship between ideal gas phase equilibrium conversion, X_{eq} , and equilibrium constant K_{xy}

$$X_{eq} = \frac{(K_{eq})^{0.5}}{1 + (K_{eq})^{0.5}}$$

In order to calculate K_{eq} it is necessary to calculate the Gibbs free energy of reaction $\Delta G_{rxn}(298K)$. The data shown in table A1-4 were used to calculate $\Delta G_{rxn}(298K)$.

Table A1-4: Thermodynamic data used to calculate reaction equilibrium for *m*-cresol and methanol to 2,5-xyleneol and water ($\Delta G_f(298K)$ and $\Delta H_f(298K)$ from Daubert *et al.*, 1999)

Compound	$\Delta G_f(298.15K)$ J / mol	$\Delta H_f(298K)$ J / mol	C_p (J / mol · K)*		
			a	b	c
<i>m</i> -Cresol	$-40.2 \cdot 10^3$	$-132 \cdot 10^3$	23.51	0.4042	$-0.1409 \cdot 10^{-3}$
Methanol	$-162.0 \cdot 10^3$	$-201 \cdot 10^3$	17.25	0.0994	$-0.0272 \cdot 10^{-3}$
2,5-Xyleneol	$-39.7 \cdot 10^3$	$-162 \cdot 10^3$	38.44	0.4674	$-0.1600 \cdot 10^{-3}$
Water	$-228.6 \cdot 10^3$	$-242 \cdot 10^3$	30.60	0.0089	$0.0016 \cdot 10^{-3}$

* C_p constants (a, b and c) values were calculated as described in section 2 of appendix 1 and given in table A1-2

Equations A1-8 to A1-10 outline the calculations to determine ΔG_{rxn} , equilibrium constant K_{eq} and heat of reaction ΔH_{rxn} at 298K using the constants given in table A1-4.

Equation A1-8: Calculation of the Gibbs free energy, ΔG_{rxn} , for *m*-cresol methylation at 298K (based on Sandler, 1989)

$$\Delta G_{rxn}(298K) = \sum_i \nu_i G_{f,i}(mol)(298K)$$

$$\Delta G_{rxn}(298K) = (\Delta G_{f,2,5-xyleneol} + \Delta G_{f,water}) - (\Delta G_{f,m-cresol} + \Delta G_{f,methanol})$$

$$\Delta G_{rxn,2,5-xyleneol}(298K) = (-39.7 \cdot 10^3 - 228.6 \cdot 10^3) - (-40.2 \cdot 10^3 - 162.0 \cdot 10^3)$$

$$\Delta G_{rxn,2,5-xyleneol}(298K) = -66.1 \cdot 10^3 \text{ J / mol}$$

Equation A1-9: Calculation of the equilibrium constant, K_{eq} , for the conversion of *m*-cresol with methanol to 2,5-xyleneol and water at 298K, using equation A1-6 and the thermodynamic data given in table A1-4

$$K_{eq,2,5-xyleneol}(298K) = e^{\frac{-\Delta G_{rxn}(298K)}{RT}} = e^{\frac{-(-66.1 \cdot 10^3)}{8.314 \cdot 298.15}} = e^{26.7} = 3.35 \cdot 10^{11}$$

Appendix 1: Thermodynamic Calculations

Equation A1-10: Calculation of the heat of reaction, ΔH_{rxn} , for *m*-cresol methylation with methanol to 2,5-xylenol and water at 298K, using the thermodynamic data in table A1-4 (based on Sandler, 1989)

$$\Delta H_{rxn}(298K) = (\Delta H_{f, 2,5\text{-xylenol}} + \Delta H_{f, \text{water}}) - (\Delta H_{f, m\text{-cresol}} + \Delta H_{f, \text{methanol}})$$
$$\Delta H_{rxn}(298K) = (-242 \cdot 10^3 - 162 \cdot 10^3) - (-201 \cdot 10^3 - 132 \cdot 10^3) = -7.10 \cdot 10^4 \text{ J/mol}$$

Equations A1-11 to A1-17 show the methods for calculating dependency of ΔH_{rxn} and K_{eq} on T.

Equation A1-11: Calculating differences of Δa , Δb and Δc of C_p constants (see equation A1-3 and table A1-4) in the methylation of *m*-cresol with methanol to 2,5-xylenol and water (based on Sandler, 1989)

$$\Delta a = (a_{2,5\text{-xylenol}} + a_{\text{water}}) - (a_{m\text{-cresol}} + a_{\text{methanol}})$$
$$\Delta a = (30.60 + 38.44) - (23.51 + 17.25) = 28.28 \text{ J/mol} \cdot \text{K}$$

And using the same method:

$$\Delta b = (0.0089 + 0.4674) - (0.0994 + 0.4042) = -0.0273 \text{ J/mol} \cdot \text{K}$$
$$\Delta c = (0.0016 \cdot 10^{-3} - 0.1600 \cdot 10^{-3}) - (-0.0272 \cdot 10^{-3} - 0.1409 \cdot 10^{-3}) = 9.70 \cdot 10^{-6} \text{ J/mol} \cdot \text{K}$$

Equation A1-12: Determining the heat of reaction at temperature T, based on the heat of reaction at 298K and using the heat capacities of reactants and products (based on Sandler, 1989)

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(298K) + \int_{T=298K}^T \Delta C_p(T') dT'$$

T' is a "dummy variable in integration" (Sandler, 1989). The above equation is expanded through substitution of the heat capacity into the integral (see equation A1-3).

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(298K) + \int_{T=298K}^T (\Delta a + \Delta b \cdot (T') + \Delta c \cdot (T')^2) dT'$$
$$\Delta H_{rxn}(T) = \Delta H_{rxn}(298K) + \Delta a(T - 298) + \frac{\Delta b}{2}(T^2 - 298^2) + \frac{\Delta c}{3}(T^3 - 298^3)$$
$$\Delta H_{rxn}(T) = -7.10 \cdot 10^4 + 28.28 \cdot (T - 298) + \frac{-0.0273}{2} \cdot (T^2 - 298^2)$$
$$+ \frac{9.70 \cdot 10^{-6}}{3} \cdot (T^3 - 298^3)$$

$K_{eq}(T)$ can now be calculated from $\Delta H_{rxn}(T)$ as follows:

Equation A1-13: Relationship between equilibrium constant, $K_{eq}(T)$, and heat of reaction, $\Delta H_{rxn}(T)$, in differential form (Sandler, 1989)

$$\frac{\partial(\ln K_{eq})}{\partial T} = \frac{\Delta H_{rxn}}{RT^2}$$

In order to calculate K_{eq} at a particular temperature, T , it is necessary to integrate equation A1-13 between standard temperature, 298K and T . Equation A1-14 illustrates this integration.

Equation A1-14: Relationship between equilibrium constant, K_{eq} , and heat of reaction, ΔH_{rxn} , both at temperature T , in differential form (Sandler, 1989)

$$\ln \left(\frac{K_{eq}(T)}{K_{eq}(298K)} \right) = \int_{298K}^T \frac{\Delta H_{rxn}(T)}{RT^2} \cdot dT$$

Replacing $\Delta H_{rxn}(T)$ by the expanded form in equation A1-12 (last line) gives equation A1-15.

Equation A1-15: Relationship between K_{eq} , ΔH_{rxn} and temperature T in differential form (Sandler, 1989)

$$\ln \left(\frac{K_{eq}(T)}{K_{eq}(298K)} \right) = \int_{298K}^T \frac{\left(\Delta H_{rxn}(298K) + \Delta a \cdot (T - 298) + \frac{\Delta b}{2} \cdot (T^2 - 298^2) + \frac{\Delta c}{3} \cdot (T^3 - 298^3) \right)}{RT^2} \cdot dT$$

For the reaction under study:

Equation A1-16: Relationship between K_{eq} , ΔH_{rxn} and temperature T in integral form (Sandler, 1989)

$$\begin{aligned} \ln \left(\frac{K_{eq}(T)}{K_{eq}(298K)} \right) = & + \frac{\Delta a}{R} \cdot \ln \left(\frac{T}{298} \right) + \frac{\Delta b}{2R} \cdot (T - 298) + \frac{\Delta c}{6R} \cdot (T^2 - 298^2) \\ & + \frac{1}{R} \left(-\Delta H_{rxn}(298) + \Delta a \cdot 298 + \frac{\Delta b}{2} \cdot 298^2 + \frac{\Delta c}{3} \cdot 298^3 \right) \cdot \left(\frac{1}{T} - \frac{1}{298} \right) \end{aligned}$$

Substituting variables Δa , Δb and Δc and $\Delta H_{rxn}(298K)$ for the reaction under study with the values listed in table A1-4 leads to equation A1-17.

Equation A1-17: Relationship between K_{eq} and temperature T for the alkylation of *m*-cresol with methanol to 2,5-xyleneol and water using variables Δa , Δb and Δc and $\Delta H_{rxn}(298K)$ from equations A1-11 and A1-10 and table A1-4

$$\begin{aligned} \ln \left(\frac{K_{xyl, 2,5-xyleneol}(T)}{K_{xyl, 2,5-xyleneol}(298K)} \right) = & + \frac{28.28}{R} \cdot \ln \left(\frac{T}{298} \right) + \frac{-0.0273}{2R} \cdot (T - 298) + \frac{9.7 \cdot 10^{-6}}{6R} \cdot (T^2 - 298^2) \\ & + \frac{1}{R} \left(-7.10 \cdot 10^4 + 28.28 \cdot 298 + \frac{-0.0273}{2} \cdot 298^2 + \frac{9.7 \cdot 10^{-6}}{3} \cdot 298^3 \right) \cdot \left(\frac{1}{T} - \frac{1}{298} \right) \end{aligned}$$

Appendix 1: Thermodynamic Calculations

By substituting a temperature of 350°C (or 623K) into equation A1-17, which was the base reaction temperature used in experiments, $K_{eq, 2,5\text{-xyleneol}}$ (623K) was calculated as $1.66 \cdot 10^5$. According to equations A1-7 this corresponds to an equilibrium conversion of 99.8 %. This can be considered as complete conversion. Table A1-5 gives ideal gas phase equilibrium conversions for *m*-cresol methylation to each of the six xyleneol isomers over a temperature range of 200-500°C. Over the entire temperature range ideal gas phase equilibrium conversions are higher than 99.2 %.

Table A1-5: Conversions at different temperatures for the alkylation of *m*-cresol with methanol to xyleneol isomers and water in ideal gas phase, based on equations A1-17

	Conversion (%) at Temperature (°C)						
	250	275	300	325	350	375	400
2,3-Xyleneol	99.8	99.8	99.7	99.6	99.5	99.3	99.2
2,4-Xyleneol	100.0	99.9	99.9	99.9	99.8	99.8	99.7
2,5-Xyleneol	99.9	99.9	99.9	99.8	99.8	99.7	99.6
2,6-Xyleneol	99.9	99.9	99.8	99.8	99.7	99.6	99.5
3,4-Xyleneol	99.9	99.8	99.7	99.7	99.6	99.5	99.4
3,5-Xyleneol	99.9	99.9	99.9	99.8	99.7	99.7	99.6

During methylation of *m*-cresol, each of the xyleneol isomers can be formed via primary or secondary reactions. Thus it is useful to compare how close the experimental distribution is to the thermodynamic distribution and to confirm whether an obtained xyleneol distribution in the product is still determined by kinetic control or not.

Equation A1-18 details the calculation used to determine the xyleneol isomers distribution in thermodynamic equilibrium in the ideal gas phase.

Equation A1-18: Calculation of the thermodynamic equilibrium molar fraction, $x_{eq,i}(T)$, of a specific xyleneol isomer (here 2,5-xyleneol) within the equilibrated xyleneol fraction in ideal gas phase

$$x_{eq, 2,5\text{-xyleneol}}(T) = \frac{1}{1 + \frac{K_{2,3\text{-xyleneol}}(T)}{K_{2,5\text{-xyleneol}}(T)} + \frac{K_{2,4\text{-xyleneol}}(T)}{K_{2,5\text{-xyleneol}}(T)} + \frac{K_{2,6\text{-xyleneol}}(T)}{K_{2,5\text{-xyleneol}}(T)} + \frac{K_{3,4\text{-xyleneol}}(T)}{K_{2,5\text{-xyleneol}}(T)} + \frac{K_{3,5\text{-xyleneol}}(T)}{K_{2,5\text{-xyleneol}}(T)}}$$

Table A1-6 gives the equilibrium distribution of the xyleneol isomers in ideal gas phase for different temperatures.

Table A1-6: Thermodynamic distribution of xlenol isomers (mol %) within the xlenol fraction at different temperatures in ideal gas phase, based on equation A1-18 and data in table A1-5

	Distribution of xlenol isomers (mol%) at Temperature (°C)						
	250	275	300	325	350	375	400
2,3-Xlenol	2.9	3.1	3.2	3.4	3.6	3.7	3.9
2,4-Xlenol	45.3	44.8	44.3	43.9	43.5	43.1	42.7
2,5-Xlenol	17.5	17.6	17.6	17.6	17.7	17.7	17.7
2,6-Xlenol	13.0	13.0	12.9	12.9	12.9	12.8	12.8
3,4-Xlenol	4.8	5.2	5.5	5.8	6.1	6.4	6.7
3,5-Xlenol	16.4	16.4	16.4	16.4	16.3	16.3	16.3

The data from table A1-6 are presented in graphical form in figures 2-4 and 2-6.

Calculating thermodynamic equilibrium for the reaction of methanol to dimethylether and water

Methanol is readily converted to dimethylether (DME) and water forming a pre-equilibrium, see equation A1-19 (Tleimat-Manzalji *et al*, 1993).

Equation A1-19: Conversion of methanol to dimethylether and water



Table A1-7 illustrates the change in moles for equation A1-19.

Table A1-7: Change in moles of reactants and products in the reaction of methanol to dimethylether (DME) and water

Compound	Moles in	Change in moles	Moles out	Mole fraction out
Methanol	2	-2X	2(1-X)	(1-X)
Dimethylether	-	X	X	X/2
Water	-	X	X	X/2
Total moles	2	-	2	1

The relationship between conversion of methanol in the above reaction (equation A1-19) and the equilibrium constant, K_{eq} , is depicted in equation A1-20.

Equation A1-20: Ideal gas phase equilibrium constant K_{eq} , and the relationship with the change in Gibbs free energy (which equals Gibbs free energy of reaction, $-\Delta G_{rxn}$) at reaction temperature T for equation A1-19 (based on Sandler, 1989)

$$K_{eq} = \frac{\left(\frac{X_{eq}}{2}\right) \cdot \left(\frac{X_{eq}}{2}\right)}{(1-X_{eq}) \cdot (1-X_{eq})} = e^{\frac{-\Delta G_{rxn}(T)}{RT}}$$

Note that this relationship is different to the relationship for the methylation of *m*-cresol to form xylenol and water, as given in equation A1-6.

Also note that the thermodynamic equilibrium is independent from pressure (see table A1-7) and therefore contains no pressure term.

The calculations performed to determine the equilibrium conversion are analogous to those that were discussed in the previous section.

Results are shown in figure 2-4, indicating that in the range of reaction temperature of interest, the equilibrium conversion of methanol to dimethylether is around 80 %.

4. Calculation of Vapour Pressures of Reactants

The vapour pressure of reactants is important for determining in which phase the reaction takes place. Equation A1-21, the Antoine equation, shows the relationship between vapour pressure and temperature (where temperature is in K).

Equation A1-21: Antoine equation, used to calculate vapour pressure of compounds at different temperatures (Perry, 1997)

$$\text{Vapour Pressure} = e^{\left[C1 + \left(\frac{C2}{T} \right) + C3 \cdot \ln(T) + C4 \cdot T^{C5} \right]}$$

Table A1-8 shows the constants that were used in calculating the vapour pressures of the feed compounds and those involved in the methanol / dimethylether pre-equilibrium. These constants were inserted into equation A1-21.

Table A1-8: Constants used to calculate the vapour pressures of various compounds (Perry, 1997)

Compound	Constants					Applicable temperature range	
	C1	C2	C3	C4	C5	T _{minimum} (°C)	T _{maximum} * (°C)
Methanol	81.768	-6876	-8.7078	$7.19 \cdot 10^{-6}$	2	-97.53	239.64
Dimethylether	44.704	-3525.6	-3.4444	$5.46 \cdot 10^{-17}$	6	-141.35	127.1
Water	73.649	-7258.2	-7.3037	$4.17 \cdot 10^{-06}$	2	0.16	374.13
m-Cresol	95.403	-10581	-10.004	$4.30 \cdot 10^{-18}$	6	12.39	432.85

*Critical temperature. Under the applied reaction conditions (base case temperature of 350°C), methanol and dimethylether were in supercritical state.

The vapour pressures are given in table A1-9. The data indicate that under the base case reaction conditions (350°C, 80 bar) the phenolic compounds (*m*-cresol and, of course, xlenols and higher phenols) are essentially in the liquid phase whereas methanol, dimethylether and water can be expected to be mostly in the vapour phase.

Appendix 1: Thermodynamic Calculations

Table A1-9: Vapour pressures of methanol, dimethylether, water and *m*-cresol (Perry, 1997)

	Vapour pressure of compounds (bar) at Temperature (°C)						
	250	275	300	325	350	375	400
Methanol	- supercritical -						
Dimethylether	- supercritical -						
Water	40	59	86	120	165	*supercritical	
<i>m</i>-Cresol	3	5	8	11	16	23	31

* $T_c=374.13^{\circ}\text{C}$

The relationships between temperature and vapour pressure of *m*-cresol is shown in figure 4-2 and those of methanol, dimethylether and water are shown in figure 4-3. Vapour pressures for other major compounds were calculated using similar methods.

Appendix 2: Experimental Data

The following tables contain raw and manipulated data that were collected from the experiments.

The designation of experiments, CM D, stands for Cresol Methylation on Rig D.

Results from experiment CM D1 are not reported because they were of very preliminary kind.

All the values reported are corrected for feed impurities and blank run results.

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Appendix 2: Experimental Data

Experiment CM D2

Start of Experiment: 11th May, 2003 at 11:40

Catalyst: H-MFI-220 (extrudates)

Si : Al ratio: 220

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g-m-cresol / g-active catalyst · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol Isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol Isomers	3-Methylanisole	"Others"
1	D2-11	73	0.37	80	351	1.0	42.4	20.1	14.6	8.0	0.3	1.0	3.1	47.2	1.8	0.0	0.5	3.2	5.6	0.3	0.0	9.5	18.1	23.4
1	D2-12	78	0.37	80	354	1.0	43.2	18.8	13.4	7.8	0.3	0.9	2.5	43.8	1.7	0.0	0.4	2.6	4.9	0.0	0.0	7.9	19.4	27.2
1	D2-13	83	0.37	80	352	1.0	43.0	19.2	13.3	8.3	0.3	0.9	2.3	44.3	1.7	0.0	0.5	2.7	4.9	0.2	0.0	8.3	20.9	24.8
1	D2-14	92	0.37	80	351	1.0	40.7	19.2	13.1	8.8	0.3	0.9	2.1	44.4	1.5	0.2	0.5	2.8	4.6	0.0	0.0	8.1	23.6	22.4
1		73-92	0.37	80	352	1.0	42.3	19.3	13.6	8.2	0.3	0.9	2.5	44.9	1.7	0.1	0.5	2.8	5.0	0.1	0.0	8.5	20.5	24.4
2	D2-17	98	1.86	80	354	1.0	29.7	14.4	5.7	10.3	0.0	0.0	0.5	31.0	0.5	0.0	0.0	1.7	1.0	0.0	0.0	2.7	56.8	9.1
2	D2-18	101	1.86	80	353	1.0	30.0	14.3	5.7	10.3	0.0	0.0	0.5	30.9	1.0	0.0	0.0	1.7	1.0	0.0	0.0	2.8	56.5	8.8
2	D2-19	103	1.86	80	353	1.0	30.4	14.2	5.6	10.3	0.0	0.0	0.5	30.7	1.2	0.0	0.0	1.8	1.0	0.0	0.0	2.8	56.0	9.4
2	D2-20	106	1.86	80	354	1.0	30.1	14.2	5.5	10.5	0.0	0.0	0.5	30.7	0.5	0.0	0.0	1.7	0.9	0.0	0.0	2.7	57.8	8.4
2	D2-21	107	1.86	80	354	1.0	30.5	14.4	5.5	10.6	0.0	0.0	0.5	31.0	0.4	0.0	0.0	1.8	1.0	0.0	0.0	2.8	57.2	8.6
2		98-107	1.86	80	354	1.0	30.2	14.3	5.6	10.4	0.0	0.0	0.5	30.8	0.7	0.0	0.0	1.7	1.0	0.0	0.0	2.7	56.8	8.8
3	D2-24	119	0.37	80	352	1.0	43.9	18.1	10.1	10.3	0.0	1.0	1.3	40.8	0.5	0.0	0.7	3.7	3.4	0.0	0.0	7.8	30.7	20.2
3	D2-25	124	0.37	80	354	1.0	45.0	17.4	9.7	9.8	0.3	0.9	1.2	39.4	1.0	0.0	0.7	3.5	3.3	0.0	0.2	7.6	30.6	21.4
3	D2-26	126	0.37	80	354	1.0	45.2	18.0	10.0	10.0	0.4	1.0	1.3	40.7	1.1	0.0	0.7	3.6	3.5	0.0	0.0	7.8	29.6	20.8
3		119-126	0.37	80	353	1.0	44.7	17.8	10.0	10.1	0.2	1.0	1.2	40.3	0.9	0.0	0.7	3.6	3.4	0.0	0.1	7.7	30.3	20.8
4	D2-31	169	0.19	80	351	1.0	48.3	19.9	13.5	9.3	0.6	1.1	2.2	46.5	1.6	0.0	0.7	3.6	5.3	0.3	0.0	10.0	17.9	24.0
4	D2-32	178	0.19	80	353	1.0	48.4	19.9	13.2	9.3	0.6	1.2	2.2	46.4	1.5	0.0	0.8	3.6	5.3	0.3	0.2	10.1	19.4	22.6
4		169-178	0.19	80	352	1.0	48.3	19.9	13.4	9.3	0.6	1.1	2.2	46.4	1.6	0.0	0.8	3.6	5.3	0.3	0.1	10.0	18.7	23.3
5	D2-34	192	0.37	80	353	1.0	39.9	16.7	9.8	9.4	0.0	0.9	1.2	37.9	1.0	0.0	0.5	2.7	3.1	0.0	0.0	6.3	35.6	19.2
5	D2-35	197	0.37	80	352	1.0	40.2	16.4	9.2	9.3	0.0	0.9	1.1	36.9	1.1	0.0	0.5	2.8	2.8	0.0	0.0	6.0	37.2	18.9
5	D2-36	198	0.37	80	352	1.0	40.2	16.2	9.0	9.4	0.0	0.8	1.1	36.4	1.4	0.0	0.5	2.9	2.8	0.0	0.0	6.2	36.7	19.3
5	D2-37	202	0.37	80	351	1.0	39.7	15.9	8.9	9.2	0.0	0.7	1.0	35.8	1.3	0.0	0.9	2.8	2.7	0.0	0.0	6.4	36.0	20.5
5		192-202	0.37	80	352	1.0	40.0	16.3	9.2	9.3	0.0	0.8	1.1	36.7	1.2	0.0	0.6	2.8	2.8	0.0	0.0	6.2	36.4	19.5

Appendix 2: Experimental Data

Experiment CM D3

Start of Experiment: 20th May, 2003 at 13:00

Catalyst: H-MFI-220 (extrudates)

Si : Al ratio: 220

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g

Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol Isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol Isomers	3-Methylanisole	"Others"
1	D3-7	43	0.37	80	354	1.0	47.6	22.4	16.2	5.9	0.5	0.9	6.1	51.9	4.8	0.4	0.4	2.5	8.9	0.5	0.0	12.6	7.5	23.1
1	D3-8	45	0.37	80	354	1.0	47.8	22.0	16.0	6.0	0.5	0.9	5.5	50.9	4.4	0.5	0.4	2.5	8.3	0.4	0.0	12.0	8.3	24.4
1	D3-9	48	0.37	80	354	1.0	47.9	21.3	15.8	6.2	0.5	0.9	4.9	49.5	3.8	0.5	0.4	2.4	7.7	0.4	0.0	11.4	9.4	25.9
1	D3-10	51	0.37	80	354	1.0	46.8	21.9	16.3	6.5	0.5	1.0	4.9	51.0	3.7	0.5	0.4	2.6	7.7	0.4	0.0	11.5	9.8	24.0
1	D3-11	55	0.37	80	350	1.0	45.5	22.0	16.5	6.7	0.5	0.9	4.7	51.3	3.3	0.5	0.4	2.5	7.6	0.3	0.0	11.3	10.3	23.8
1	D3-12	66	0.37	80	354	1.0	44.7	21.6	16.3	7.1	0.5	0.9	3.9	50.3	2.8	0.5	0.4	2.5	6.7	0.3	0.0	10.4	12.6	24.0
1	D3-13	69	0.37	80	353	1.0	45.3	21.3	16.0	7.2	0.5	0.9	3.6	49.5	3.0	0.5	0.4	2.6	6.6	0.3	0.0	10.4	13.2	23.9
1		43 - 69	0.37	80	353	1.0	46.5	21.8	16.2	6.5	0.5	0.9	4.8	50.6	3.7	0.5	0.4	2.5	7.7	0.4	0.0	11.4	10.1	24.2
2	D3-18	76	1.86	80	352	1.0	32.2	14.0	6.5	9.9	0.0	0.0	0.5	30.9	0.6	0.0	0.6	1.4	1.1	0.0	0.0	3.2	55.6	9.8
2	D3-19	77	1.86	80	353	1.0	33.8	13.8	6.0	9.6	0.0	0.0	0.5	29.9	0.6	0.0	0.5	1.5	1.0	0.0	0.0	3.0	51.9	14.6
2	D3-20	80	1.86	80	353	1.0	33.2	13.8	6.1	10.0	0.0	0.0	0.5	30.5	0.4	0.0	0.5	1.6	1.1	0.0	0.0	3.1	54.5	11.5
2	D3-21	83	1.86	80	354	1.0	33.1	14.0	6.1	10.2	0.0	0.0	0.5	30.8	0.5	0.0	0.5	1.6	1.0	0.0	0.0	3.1	55.1	10.5
2		76 - 83	1.86	80	354	1.0	33.1	13.9	6.2	9.9	0.0	0.0	0.5	30.5	0.5	0.0	0.5	1.5	1.0	0.0	0.0	3.1	54.3	11.6
3	D3-24	98	0.37	80	353	1.0	46.7	18.4	11.3	9.6	0.4	1.1	1.1	41.9	1.2	0.0	0.8	3.5	3.9	0.0	0.3	8.5	25.0	23.4
3	D3-25	102	0.37	80	353	1.0	45.5	19.7	12.0	10.0	0.0	1.2	1.3	44.2	1.3	0.0	0.8	3.6	4.2	0.0	0.0	8.6	25.1	20.8
3	D3-26	106	0.37	80	353	1.0	46.1	19.4	12.0	9.7	0.4	1.1	1.3	43.9	1.4	0.0	0.8	3.6	4.2	0.0	0.3	8.8	23.8	22.1
3		98 - 106	0.37	80	353	1.0	46.1	19.2	11.8	9.8	0.3	1.1	1.2	43.3	1.3	0.0	0.8	3.6	4.1	0.0	0.2	8.6	24.7	22.1
4	D3-29	129	0.19	80	351	1.0	52.5	22.1	14.5	9.3	0.7	1.2	2.8	50.6	2.0	0.0	1.0	4.1	6.3	0.4	0.2	12.0	12.1	23.2
4	D3-30	140	0.19	80	353	1.0	51.8	22.3	14.9	9.2	0.7	1.1	3.1	51.4	2.5	0.0	1.0	3.9	6.6	0.4	0.2	12.1	11.2	22.7
4	D3-31	143	0.19	80	349	1.0	51.2	21.6	14.9	8.8	0.7	1.1	3.3	50.5	2.7	0.0	1.0	3.7	6.5	0.4	0.2	11.7	10.7	24.4
4	D3-32	149	0.19	80	352	1.0	49.9	22.2	15.5	9.0	0.6	1.1	3.2	51.7	2.4	0.0	1.1	3.5	6.5	0.3	0.3	11.6	12.0	22.3
4		129 - 149	0.19	80	352	1.0	51.3	22.0	15.0	9.1	0.7	1.1	3.1	51.1	2.4	0.0	1.0	3.8	6.5	0.4	0.2	11.9	11.5	23.2
5	D3-36	169	0.37	80	352	1.0	43.6	17.9	11.8	9.0	0.3	1.0	1.4	41.4	2.1	0.0	1.4	2.8	3.7	0.0	0.3	8.1	25.9	22.6
5	D3-37	177	0.37	80	352	1.0	43.1	18.2	11.9	9.3	0.3	1.0	1.2	42.0	1.6	0.0	1.4	2.9	3.7	0.0	0.3	8.3	27.0	21.2
5	D3-38	189	0.37	80	353	1.0	44.4	17.7	11.3	9.0	0.4	1.0	1.3	40.7	1.2	0.0	1.4	2.9	3.6	0.0	0.2	8.0	26.6	23.5
5	D3-39	191	0.37	80	353	1.0	42.9	18.1	11.5	9.4	0.4	1.0	1.4	41.9	1.0	0.0	1.4	3.0	3.6	0.0	0.2	8.2	28.2	20.7
5		169 - 191	0.37	80	353	1.0	43.5	18.0	11.6	9.2	0.4	1.0	1.3	41.5	1.5	0.0	1.4	2.9	3.6	0.0	0.2	8.2	26.9	22.0

Appendix 2: Experimental Data

Experiment CM D4

Start of Experiment: 29th May, 2003 at 10:30

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} * h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D4-14	83.9	0.37	40	352	1.0	62.7	17.0	10.6	6.0	0.9	1.9	9.1	45.4	11.2	0.3	0.8	4.4	11.0	1.1	0.3	17.9	2.2	23.3
1	D4-15	94.3	0.37	40	354	1.0	62.3	17.1	10.6	6.1	0.9	1.9	9.1	45.8	11.0	0.3	0.8	4.5	11.2	1.1	0.3	18.3	2.4	22.6
1	D4-16	97.8	0.37	40	354	1.0	62.0	17.1	11.0	6.1	0.9	1.9	9.1	46.2	11.2	0.3	0.8	4.5	11.0	1.1	0.3	18.0	2.5	22.2
1	84-98		0.37	40	354	1.0	62.4	17.1	10.7	6.1	0.9	1.9	9.1	45.8	11.1	0.3	0.8	4.5	11.1	1.1	0.3	18.0	2.3	22.7
2	D4-20	102.8	1.86	40	353	1.0	37.0	18.3	18.6	8.8	0.0	0.7	3.1	49.5	1.9	0.3	0.3	2.4	6.4	0.0	0.0	9.4	17.8	21.4
2	D4-21	104.5	1.86	40	354	1.0	36.8	18.2	18.6	9.1	0.0	0.7	2.7	49.2	1.5	0.3	0.3	2.3	5.9	0.0	0.0	8.8	19.0	21.5
2	D4-22	106.7	1.86	40	355	1.0	37.8	18.2	18.6	9.0	0.0	0.7	2.8	49.3	1.6	0.3	0.3	2.4	6.0	0.0	0.0	9.0	18.1	22.0
2	D4-23	108.1	1.86	40	355	1.0	38.1	18.1	18.4	9.1	0.0	0.7	2.7	49.0	1.5	0.3	0.4	2.4	6.0	0.0	0.0	9.1	18.4	21.9
2	D4-24	109.7	1.86	40	354	1.0	38.1	18.3	18.4	9.1	0.0	0.7	2.7	49.1	1.5	0.3	0.4	2.4	6.0	0.0	0.0	9.1	18.4	21.9
2	103-110		1.86	40	354	1.0	37.6	18.2	18.5	9.0	0.0	0.7	2.8	49.2	1.6	0.3	0.3	2.4	6.1	0.0	0.0	9.1	18.3	21.7
3	D4-31	128	0.93	40	356	1.0	47.7	19.6	16.8	8.2	0.4	1.0	5.5	51.4	3.9	0.3	0.5	3.4	9.4	0.4	0.2	14.2	8.5	21.9
3	D4-32	133	0.93	40	356	1.0	48.3	19.1	16.9	8.1	0.4	1.0	5.3	50.7	3.8	0.3	0.5	3.4	9.6	0.3	0.2	14.5	8.0	23.0
3	D4-33	134.2	0.93	40	353	1.0	47.2	19.6	16.9	8.2	0.4	1.0	5.3	51.4	3.6	0.3	0.5	3.4	9.4	0.4	0.2	14.2	8.7	22.2
3	D4-34	142.6	0.93	40	354	1.0	46.9	19.1	17.5	8.3	0.5	0.9	4.9	51.2	3.4	0.3	0.5	3.6	8.8	0.4	0.2	13.8	9.0	22.6
3	128-143		0.93	40	354	1.0	47.5	19.3	17.0	8.2	0.4	0.9	5.3	51.2	3.7	0.3	0.5	3.4	9.3	0.4	0.2	14.2	8.6	22.4
4	D4-36	144.3	3.72	40	351	1.0	25.6	15.2	15.8	9.6	0.0	0.3	1.0	42.0	1.0	0.0	0.0	1.4	3.1	0.0	0.0	4.4	36.7	16.0
4	D4-37	146.3	3.72	40	350	1.0	25.2	14.4	14.9	9.8	0.0	0.0	0.8	39.9	1.0	0.0	0.0	1.2	2.4	0.0	0.0	3.5	40.6	14.9
4	D4-38	147.8	3.72	40	352	1.0	24.9	14.4	14.8	9.9	0.0	0.0	0.7	39.8	1.0	0.0	0.0	1.2	2.3	0.0	0.0	3.4	41.4	14.4
4	D4-39	148.8	3.72	40	353	1.0	24.8	14.6	15.0	10.0	0.0	0.0	0.7	40.2	0.9	0.0	0.0	1.2	2.4	0.0	0.0	3.6	40.3	14.9
4	D4-40	149.3	3.72	40	350	1.0	24.7	14.8	15.0	9.9	0.0	0.0	0.7	40.4	0.9	0.0	0.0	1.2	2.5	0.0	0.0	3.7	39.7	15.3
4	144-149		3.72	40	350	1.0	25.0	14.7	15.1	9.9	0.0	0.1	0.8	40.5	0.9	0.0	0.0	1.2	2.5	0.0	0.0	3.7	39.7	15.1
5	D4-44	152.2	3.72	80	355	1.0	32.9	16.2	19.4	11.4	0.0	0.5	0.7	48.2	0.7	0.4	0.2	1.8	3.2	0.0	0.0	5.7	25.4	20.0
5	D4-45	153.7	3.72	80	355	1.0	33.2	16.5	19.3	11.4	0.0	0.5	0.8	48.4	0.7	0.4	0.2	1.8	3.3	0.0	0.0	5.7	25.8	19.4
5	D4-46	154.9	3.72	80	356	1.0	33.6	16.5	19.4	11.4	0.0	0.5	0.8	48.5	0.7	0.4	0.2	1.9	3.4	0.0	0.0	5.9	24.9	20.0
5	D4-47	155.7	3.72	80	355	1.0	34.0	16.5	19.4	11.2	0.0	0.5	0.8	48.5	0.6	0.4	0.2	1.9	3.6	0.0	0.0	6.1	24.3	20.5
5	152-156		3.72	80	355	1.0	33.4	16.4	19.4	11.4	0.0	0.5	0.8	48.4	0.7	0.4	0.2	1.9	3.4	0.0	0.0	5.8	25.1	20.0

Appendix 2: Experimental Data

Experiment CM D4 (continued)

Start of Experiment: 29th May, 2003 at 10:30

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Number	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
6	D4-49	166.2	0.37	80	351	1.0	63.9	16.4	13.6	8.1	0.7	1.1	5.1	45.1	3.2	0.7	1.1	5.3	11.9	0.7	0.3	20.0	3.7	28.1
6	D4-50	168.4	0.37	80	348	1.0	63.4	16.2	13.5	7.9	0.6	1.0	5.5	44.8	4.0	0.6	1.0	5.4	12.1	0.7	0.3	20.1	3.0	28.1
6	D4-51	170.6	0.37	80	348	1.0	62.0	16.7	13.7	8.0	0.7	1.1	5.6	45.8	3.7	0.5	1.0	5.2	11.8	0.7	0.3	19.5	2.9	28.1
6	D4-52	173.4	0.37	80	353	1.0	60.7	17.2	14.0	8.2	0.7	1.1	5.9	47.0	4.1	0.5	0.9	5.3	11.9	0.6	0.3	19.6	2.8	26.5
6	D4-53	175.3	0.37	80	353	1.0	60.6	17.5	13.6	8.0	0.8	1.2	6.7	47.8	4.9	0.5	1.0	5.2	12.3	0.7	0.2	19.9	2.8	24.5
6	D4-54	180.3	0.37	80	354	1.0	62.0	16.6	13.4	7.7	0.8	1.2	7.0	46.6	5.5	0.5	1.0	5.4	12.6	0.8	0.3	20.5	2.4	25.0
6	D4-55	190.6	0.37	80	353	1.0	61.4	16.9	13.0	7.5	0.8	1.3	7.1	46.5	6.5	0.4	0.9	5.0	12.5	0.8	0.2	20.0	2.6	24.4
6	D4-56	193.2	0.37	80	354	1.0	59.7	17.5	13.4	7.6	0.8	1.4	7.7	48.4	6.7	0.4	0.9	5.2	12.6	0.8	0.2	20.3	2.8	21.8
6	D4-57	197.3	0.37	80	356	1.0	61.0	16.7	12.8	7.2	0.8	1.4	7.4	46.4	6.2	0.3	0.9	5.1	12.4	0.8	0.3	19.8	2.7	24.9
6	D4-58	198.7	0.37	80	355	1.0	59.7	17.3	13.0	7.4	0.9	1.5	8.0	48.1	7.2	0.3	0.9	4.9	12.4	0.9	0.2	19.6	2.7	22.3
6	166-199		0.37	80	355	1.0	61.4	16.9	13.4	7.8	0.8	1.2	6.6	46.7	5.2	0.5	1.0	5.2	12.3	0.7	0.3	19.9	2.8	25.4
7	D4-65	245	0.43	80	353	0.5	45.8	18.1	12.9	6.4	1.0	2.1	10.4	50.8	18.0	0.3	0.4	3.1	9.5	0.6	0.0	13.9	2.4	14.9
7	D4-66	249.9	0.43	80	352	0.5	45.1	18.3	13.5	6.6	0.9	2.0	10.2	51.5	17.2	0.2	0.4	3.1	9.5	0.6	0.2	14.0	2.6	14.7
7	D4-67	251.7	0.43	80	352	0.5	45.2	18.4	13.9	6.7	0.9	1.9	10.1	51.8	16.3	0.3	0.4	3.1	9.6	0.6	0.2	14.2	2.7	14.9
7	D4-68	262.4	0.43	80	350	0.5	45.2	18.1	14.0	6.7	0.8	1.7	9.7	51.0	15.1	0.3	0.4	3.0	9.4	0.5	0.0	13.7	2.8	17.4
7	D4-69	264.2	0.43	80	350	0.5	44.6	18.7	14.7	7.0	0.8	1.7	9.5	52.4	14.6	0.2	0.5	3.2	9.6	0.5	0.2	14.1	2.9	16.0
7	D4-70	265.2	0.43	80	350	0.5	44.6	18.8	14.9	7.1	0.8	1.7	9.6	52.9	14.0	0.2	0.5	3.2	9.9	0.5	0.2	14.4	2.9	15.8
7	245-265		0.43	80	350	0.5	45.1	18.4	14.0	6.8	0.9	1.8	9.9	51.7	15.9	0.2	0.4	3.1	9.6	0.6	0.1	14.1	2.7	15.6
8	D4-83	342.6	0.29	80	354	2.0	58.9	15.1	14.6	7.1	0.5	0.9	2.9	41.1	2.1	0.5	0.7	3.9	1.3	0.5	0.3	15.2	7.6	33.9
8	D4-84	349.2	0.29	80	354	2.0	57.9	15.3	14.9	7.3	0.3	0.9	2.6	41.3	1.2	0.5	0.6	3.9	8.9	0.4	0.2	14.6	8.3	34.7
8	D4-85	359.3	0.29	80	354	2.0	55.3	15.8	15.5	7.6	0.4	0.8	2.6	42.7	1.3	0.6	0.6	3.6	8.5	0.4	0.2	13.9	8.8	33.2
8	D4-86	363.2	0.29	80	354	2.0	54.9	15.5	15.1	7.5	0.3	0.8	2.4	41.6	1.0	0.5	0.6	3.7	8.4	0.4	0.2	13.9	9.4	34.2
8	D4-87	367.2	0.29	80	354	2.0	54.5	15.4	15.2	7.5	0.3	0.8	2.3	41.5	1.1	0.5	0.6	3.7	8.1	0.3	0.2	13.5	9.2	34.6
8	D4-88	375.6	0.29	80	355	2.0	53.1	15.5	15.3	7.6	0.3	0.8	2.2	41.6	0.7	0.5	0.6	3.6	7.9	0.3	0.2	13.2	9.9	34.5
8	D4-89	385.1	0.29	80	354	2.0	52.0	15.5	15.3	7.6	0.2	0.8	2.1	41.6	1.0	0.5	0.6	3.5	7.5	0.3	0.2	12.7	10.5	34.2
8	D4-90	390	0.29	80	354	2.0	51.2	15.3	15.2	7.6	0.2	0.7	1.9	41.1	0.9	0.3	0.6	3.4	7.2	0.3	0.2	12.0	10.9	35.1
8	D4-91	396.3	0.29	80	354	2.0	49.6	15.6	15.4	7.7	0.2	0.7	1.9	41.6	0.9	0.3	0.5	3.4	7.2	0.3	0.2	11.9	11.5	34.1
8	342-396		0.29	80	354	2.0	54.2	15.5	15.2	7.5	0.3	0.8	2.3	41.6	1.2	0.5	1.5	3.6	7.2	0.4	0.2	13.4	9.6	34.3
9	D4-100	473.8	0.37	80	354	1.0	31.1	17.2	16.9	8.3	0.5	0.6	3.4	46.9	3.2	0.3	0.7	3.0	7.0	0.4	0.2	11.7	12.6	25.6
9	D4-101	478.4	0.37	80	356	1.0	32.0	16.7	17.2	8.5	0.4	0.4	2.8	46.0	3.1	0.5	0.6	3.1	6.7	0.4	0.2	11.4	12.3	27.2
9	D4-102	482.2	0.37	80	357	1.0	31.9	16.9	17.3	8.7	0.4	0.4	2.5	46.1	2.0	0.5	0.6	3.1	6.7	0.3	0.2	11.4	13.9	26.7
9	474-482		0.37	80	357	1.0	31.7	16.9	17.1	8.5	0.4	0.4	2.9	46.3	2.7	0.4	0.6	3.1	6.8	0.4	0.2	11.5	12.9	26.5

Appendix 2: Experimental Data

Experiment CM D5

Start of Experiment: 20th June, 2003 at 10:30

Catalyst: Blank Run

Si : Al ratio: -

Pore Diameter (Å): -

Total Mass of Catalyst (g): - g

Pump rate (ml / min): 0.02 Mass of Active Catalyst (g): - g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} * h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D5-10	78	.	80	354	1.0	1.3	18.4	5.2	7.1	0.0	0.0	0.0	30.7	42.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.8	5.1
1	D5-11	89	.	80	352	1.0	1.4	18.6	5.4	7.2	0.0	0.0	0.0	31.1	39.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.1	4.8
1	D5-12	93	.	80	353	1.0	1.3	17.3	5.0	6.8	0.0	0.0	0.0	29.2	41.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	24.1	5.1
1	D5-13	97	.	80	354	1.0	1.3	19.1	0.0	7.9	0.0	0.0	0.0	27.0	45.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	27.4	0.0
1		78-97		80	353	1.0	1.4	18.1	5.2	7.0	0.0	0.0	0.0	30.3	41.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23.3	5.0

Appendix 2: Experimental Data

Experiment CM D6

Start of Experiment: 27th June, 2003 at 11:30

Catalyst: H-BEA-150 (powder)

Si : Al ratio: 150

Pore Diameter (Å): 5.6 x 5.6 <-> 6.6 x 6.7

Total Mass of Catalyst (g): 2.4 g Mass of Active Catalyst (g): 2.4 g

Sample information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D6-7	55	0.37	80	355	1.0	71.7	13.8	8.5	7.1	3.9	2.1	7.2	42.6	7.5	4.1	6.4	4.7	6.1	3.7	1.3	26.3	0.2	23.4
1	D6-8	58	0.37	80	352	1.0	71.3	13.7	9.0	7.8	3.4	1.7	6.8	42.4	5.1	4.7	6.6	4.8	6.4	3.7	1.4	27.7	0.3	24.5
1	D6-9	64	0.37	80	357	1.0	70.8	13.9	9.2	8.1	3.2	1.6	6.7	42.8	5.0	4.9	6.6	4.9	6.5	3.7	0.1	26.8	0.3	25.2
1	D6-10	69	0.37	80	348	1.0	71.4	13.3	9.6	8.6	2.6	1.2	5.8	41.2	3.8	5.4	6.5	5.1	6.8	3.3	1.5	28.7	0.5	25.9
1	D6-11	73	0.37	80	348	1.0	71.2	13.1	9.6	8.8	2.2	1.1	5.3	40.1	3.2	5.7	6.3	5.2	6.9	3.1	1.5	28.6	1.0	27.1
1	D6-11	55-73	0.37	80	348	1.0	71.3	13.6	9.2	8.1	3.1	1.5	6.4	41.8	4.9	4.9	6.5	4.9	6.5	3.5	1.2	27.6	0.5	25.2
2	D6-23	95	1.86	80	352	1.0	51.6	15.2	13.3	13.9	0.9	0.2	2.5	46.0	1.6	3.1	3.5	4.8	6.0	1.1	1.2	19.8	12.2	20.4
2	D6-24	97	1.86	80	350	1.0	52.4	14.6	13.1	13.6	0.8	0.2	2.4	44.7	1.6	3.1	3.4	4.8	6.0	1.0	1.2	19.5	12.2	22.0
2	D6-25	98	1.86	80	352	1.0	52.2	14.8	13.2	13.7	0.8	0.1	2.3	45.0	1.5	3.1	3.4	4.8	6.0	0.9	1.2	19.6	10.7	23.2
2	D6-25	95-98	1.86	80	352	1.0	52.1	14.9	13.2	13.8	0.8	0.2	2.4	45.2	1.6	3.1	3.5	4.8	6.0	1.0	1.2	19.6	11.7	21.9
3	D6-29	107	0.93	80	358	1.0	56.5	14.3	12.9	13.1	1.1	0.3	3.1	44.7	3.5	4.0	4.2	5.0	6.6	1.6	1.3	22.8	7.1	21.9
3	D6-30	118	0.93	80	358	1.0	56.6	14.6	12.3	13.0	1.0	0.3	3.1	44.3	2.0	3.9	4.1	4.9	6.3	1.6	1.3	22.1	8.7	22.9
3	D6-31	120	0.93	80	352	1.0	56.8	14.2	12.5	13.1	1.0	0.3	3.1	44.1	1.8	3.9	4.1	5.0	6.4	1.5	1.3	22.2	9.2	22.7
3	D6-32	123	0.93	80	351	1.0	57.1	14.0	12.4	12.9	1.0	0.3	3.0	43.6	1.8	4.0	4.1	4.9	6.4	1.5	1.4	22.2	8.7	23.7
3	D6-34	125	0.93	80	352	1.0	56.0	14.3	12.5	13.1	1.0	0.3	3.2	44.5	1.8	3.7	4.0	4.9	6.2	1.5	1.3	21.8	9.8	22.1
3	D6-35	127	0.93	80	353	1.0	56.0	14.5	12.7	13.2	1.0	0.3	3.2	45.0	1.8	3.8	4.1	5.0	6.4	1.5	1.3	22.1	9.1	22.0
3	D6-35	107-128	0.93	80	353	1.0	56.5	14.3	12.6	13.1	1.0	0.3	3.1	44.4	2.1	3.9	4.1	5.0	6.4	1.5	1.3	22.2	8.8	22.6
4	D6-42	204	0.19	80	349	1.0	58.8	15.2	12.3	12.5	1.1	0.4	3.0	44.4	1.9	4.3	4.3	5.5	6.7	1.5	1.3	23.5	7.4	22.9
4	D6-43	214	0.19	80	350	1.0	58.9	15.3	12.3	12.4	1.2	0.4	3.2	44.8	1.9	4.5	4.6	5.5	6.8	1.6	1.4	24.4	6.1	22.8
4	D6-44	234	0.19	80	351	1.0	59.0	15.2	12.1	12.2	1.3	0.5	3.4	44.6	2.1	4.5	4.6	5.3	6.6	1.8	1.3	24.2	5.9	23.1
4	D6-45	242	0.19	80	349	1.0	59.0	15.2	12.3	12.1	1.4	0.5	3.6	45.1	2.4	4.7	4.8	5.3	6.7	1.9	1.4	24.9	4.7	23.0
4	D6-46	253	0.19	80	353	1.0	59.1	15.2	12.3	12.2	1.4	0.5	3.7	45.3	2.2	4.8	4.9	5.4	6.8	2.0	1.4	25.1	4.9	22.4
4	D6-47	262	0.19	80	350	1.0	59.3	15.0	12.1	11.9	1.4	0.6	3.8	44.7	2.5	4.7	4.9	5.2	6.6	2.0	1.3	24.8	4.7	23.4
4	D6-48	269	0.19	80	351	1.0	58.8	15.2	12.0	12.0	1.4	0.6	3.8	45.0	2.6	4.6	4.9	5.2	6.6	2.1	1.3	24.7	4.9	22.8
4	D6-49	272	0.19	80	351	1.0	59.1	15.1	12.1	12.0	1.4	0.6	3.8	45.0	2.6	4.7	4.9	5.3	6.6	2.1	1.3	24.9	4.7	22.9
4	D6-49	203-272	0.19	80	351	1.0	59.0	15.2	12.2	12.1	1.3	0.5	3.5	44.9	2.3	4.6	4.7	5.3	6.7	1.9	1.3	24.6	5.4	22.9
5	D6-53	234	0.37	80	351	1.0	57.4	14.8	12.4	12.7	1.2	0.4	3.6	45.2	2.3	4.4	4.5	5.0	6.4	1.8	1.3	23.4	7.0	22.1
5	D6-54	242	0.37	80	351	1.0	57.4	14.8	12.3	12.7	1.2	0.4	3.5	44.9	2.1	4.3	4.4	5.0	6.4	1.8	1.3	23.2	7.5	22.3
5	D6-55	253	0.37	80	351	1.0	57.5	14.6	12.3	12.6	1.2	0.4	3.4	44.5	2.2	4.2	4.3	5.0	6.3	1.8	1.3	23.0	7.6	22.8
5	D6-56	262	0.37	80	353	1.0	57.4	14.5	12.3	12.6	1.2	0.4	3.4	44.3	2.5	4.2	4.3	5.0	6.3	1.8	1.3	22.8	7.8	22.6
5	D6-57	269	0.37	80	352	1.0	57.6	14.5	12.3	12.5	1.2	0.4	3.4	44.3	2.1	4.3	4.3	5.0	6.3	1.8	1.3	23.0	7.6	23.0
5	D6-57	234-269	0.37	80	352	1.0	57.5	14.6	12.3	12.6	1.2	0.4	3.4	44.6	2.3	4.3	4.4	5.0	6.3	1.8	1.3	23.1	7.5	22.5

Appendix 2: Experimental Data

Experiment CM D7

Start of Experiment: 16th July, 2003 at 13:30

Catalyst: H-FER-20 (extrudates)

Si : Al ratio: 20

Pore Diameter (Å): 3.5 x 4.8 <-> 4.2 x 5.4

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} * h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D7-14	116	0.37	80	351	1.0	12.1	13.8	7.4	5.9	0.0	0.0	0.0	27.1	1.1	0.0	0.0	1.3	1.5	0.0	0.0	2.9	58.3	10.6
1	D7-15	124	0.37	80	351	1.0	13.3	13.6	7.4	5.9	0.0	0.0	0.0	26.9	1.9	0.8	0.0	1.3	1.6	0.0	0.0	3.7	51.4	16.1
1	D7-16	127	0.37	80	352	1.0	12.8	14.5	7.7	6.4	0.0	0.0	0.0	28.6	4.0	0.0	0.0	1.4	1.8	0.0	0.0	3.2	53.2	11.1
1	D7-17	138	0.37	80	352	1.0	12.4	14.9	7.9	6.5	0.0	0.0	0.0	29.3	1.1	0.0	0.0	1.6	1.8	0.0	0.0	3.3	58.1	8.2
1	D7-18	144	0.37	80	352	1.0	12.1	15.1	8.0	6.7	0.0	0.0	0.0	29.8	3.1	0.0	0.0	1.5	1.9	0.0	0.0	3.4	55.5	8.3
1	D7-19	153	0.37	80	352	1.0	12.4	14.3	7.5	6.4	0.0	0.0	0.0	28.2	1.9	0.0	0.0	1.5	1.8	0.0	0.0	3.3	56.6	10.1
1	D7-20	162	0.37	80	352	1.0	13.1	14.5	7.6	6.5	0.0	0.0	0.6	29.2	1.0	0.0	0.0	1.6	1.8	0.0	0.0	3.4	57.7	8.7
1	D7-21	180	0.37	80	360	1.0	11.7	15.9	7.4	6.7	0.0	0.0	0.7	30.8	1.3	0.0	0.0	1.8	1.9	0.0	0.0	3.7	56.3	7.9
1	D7-21	127-180	0.37	80	353	1.0	12.5	14.6	7.6	6.4	0.0	0.0	0.2	28.7	1.9	0.1	0.0	1.5	1.8	0.0	0.0	3.3	55.9	10.1
2	D7-22	187	0.37	80	359	1.0	10.0	16.5	8.7	7.5	0.0	0.0	0.0	32.7	1.6	0.8	0.0	2.3	2.5	0.0	0.0	5.6	49.5	10.6
2	D7-23	194	0.37	80	357	1.0	9.5	15.8	8.2	7.3	0.0	0.0	0.8	32.1	1.7	0.8	0.0	2.1	2.3	0.0	0.0	5.2	49.3	11.6
2	D7-24	204	0.37	80	357	1.0	9.5	14.8	7.6	6.9	0.0	0.0	0.0	29.2	1.7	0.7	0.0	2.0	2.2	0.0	0.0	5.0	53.2	10.8
2	D7-25	211	0.37	80	357	1.0	9.0	14.6	7.6	6.9	0.0	0.0	0.0	29.2	1.8	0.0	0.0	2.0	2.2	0.0	0.0	4.2	55.0	9.9
2	D7-26	224	0.37	80	357	1.0	8.9	14.3	7.3	6.8	0.0	0.0	0.0	28.5	1.9	0.0	0.0	1.9	2.1	0.0	0.0	3.9	56.3	9.4
2	D7-26	187-224	0.37	80	357	1.0	9.4	15.2	7.9	7.1	0.0	0.0	0.2	30.3	1.8	0.4	0.0	2.1	2.3	0.0	0.0	4.8	52.7	10.5
3	D7-28	250	0.19	80	356	1.0	14.8	14.9	7.5	6.9	0.0	0.0	0.8	30.1	1.1	0.7	0.5	2.2	2.3	0.0	0.0	5.7	51.6	11.5
3	D7-29	261	0.19	80	356	1.0	13.9	15.6	7.7	7.1	0.0	0.0	0.9	31.4	1.2	0.0	0.0	2.2	2.3	0.0	0.0	4.5	55.2	7.7
3	D7-30	272	0.19	80	356	1.0	14.5	14.8	7.5	6.8	0.0	0.0	1.0	30.0	2.4	0.7	0.0	2.2	2.1	0.0	0.0	5.0	50.1	12.4
3	D7-31	283	0.19	80	356	1.0	14.6	14.2	7.4	6.5	0.0	0.0	0.9	29.0	1.1	1.3	0.0	2.1	2.4	0.0	0.0	5.7	49.1	15.1
3	D7-31	250-283	0.19	80	356	1.0	14.5	14.9	7.5	6.8	0.0	0.0	0.9	30.1	1.5	0.7	0.1	2.2	2.3	0.0	0.0	5.2	51.5	11.7
4	D7-34	314	0.19	80	406	1.0	12.0	27.8	7.8	10.3	0.7	0.0	2.6	49.2	3.2	1.1	1.4	4.1	3.4	0.0	0.0	10.0	20.6	17.0
4	D7-35	326	0.19	80	400	1.0	11.4	28.4	8.1	10.1	0.0	0.0	2.6	49.2	1.7	1.8	1.6	4.7	4.0	0.7	0.0	12.7	20.4	16.0
4	D7-36	332	0.19	80	391	1.0	12.6	28.3	8.1	9.7	0.7	0.0	2.5	49.3	2.0	1.7	1.5	4.7	4.1	0.7	0.0	12.7	20.6	15.4
4	D7-37	341	0.19	80	399	1.0	12.2	30.1	8.8	10.4	0.0	0.0	2.2	51.4	1.6	0.9	1.3	4.2	3.8	0.0	0.0	10.1	22.6	14.2
4	D7-38	351	0.19	80	399	1.0	12.3	30.8	9.1	10.7	0.7	0.0	2.2	53.6	1.6	0.7	1.4	4.1	3.5	0.0	0.0	9.8	22.8	12.2
4	D7-39	360	0.19	80	398	1.0	13.2	29.6	8.9	10.6	0.9	0.0	2.3	52.3	3.2	0.6	1.4	3.8	3.4	0.6	0.0	9.8	21.9	12.9
4	D7-39	314-360	0.19	80	399	1.0	12.3	29.2	8.5	10.3	0.5	0.0	2.4	50.8	2.2	1.1	1.4	4.3	3.7	0.3	0.0	10.9	21.5	14.6

Appendix 2: Experimental Data

Experiment CM D8

Start of Experiment: 5th August, 2003 at 11:00

Catalyst: H-MOR-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 2.6 x 5.7 <-> 6.5 x 7.0

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D8-11	72	0.37	80	352	1.0	21.8	18.4	11.5	7.8	0.0	0.0	0.7	38.4	3.3	0.4	0.4	1.3	2.1	0.0	0.4	4.7	35.5	18.1
1	D8-12	95	0.37	80	352	1.0	23.5	18.4	10.8	8.2	0.0	0.0	0.6	38.0	3.8	0.0	0.5	1.5	2.2	0.0	0.0	4.2	38.6	15.4
1	D8-13	112	0.37	80	351	1.0	23.3	16.8	9.9	7.9	0.0	0.0	0.6	35.2	3.9	0.4	0.9	1.5	2.0	0.0	0.0	4.8	42.4	13.6
1	D8-14	118	0.37	80	352	1.0	22.6	16.0	9.4	7.7	0.0	0.0	0.6	33.7	4.0	0.0	0.8	1.6	1.9	0.0	0.0	4.3	45.1	13.0
1		72-118	0.37	80	352	1.0	22.8	17.4	10.4	7.9	0.0	0.0	0.6	36.3	3.8	0.2	0.7	1.5	2.1	0.0	0.1	4.5	40.4	15.0
2	D8-16	143	0.19	80	353	1.0	27.7	17.6	10.1	8.1	0.4	0.0	0.7	36.9	1.6	0.4	0.7	2.1	2.5	0.0	0.0	5.7	38.9	16.9
2	D8-17	158	0.19	80	352	1.0	27.9	16.7	9.4	7.8	0.4	0.0	0.7	34.9	0.9	0.5	0.6	2.0	2.4	0.0	0.0	5.6	40.2	18.5
2	D8-18	165	0.19	80	354	1.0	27.1	17.2	9.6	8.0	0.4	0.0	0.7	36.0	1.4	0.5	0.7	2.1	2.6	0.0	0.0	5.9	40.3	16.5
2		143-165	0.19	80	353	1.0	27.6	17.2	9.7	8.0	0.4	0.0	0.7	35.9	1.3	0.5	0.7	2.1	2.5	0.0	0.0	5.7	39.8	17.3
3	D8-26	239	0.19	80	353	1.0	20.3	16.6	8.8	7.8	0.0	0.0	0.7	34.0	1.8	0.6	0.6	2.1	2.4	0.0	0.0	5.7	45.8	12.8
3	D8-27	256	0.19	80	354	1.0	20.4	16.3	8.4	7.7	0.0	0.0	0.7	33.0	1.2	0.6	0.6	2.2	2.3	0.0	0.0	5.7	48.2	11.9
3	D8-28	267	0.19	80	352	1.0	18.0	18.1	9.4	8.6	0.0	0.0	0.6	36.7	5.2	0.7	0.6	2.3	2.6	0.0	0.0	6.2	40.3	11.6
3	D8-29	282	0.19	80	354	1.0	19.6	15.8	8.0	7.4	0.0	0.0	0.7	31.8	2.5	0.6	3.3	2.2	2.3	0.0	0.0	8.4	47.1	10.2
3		239-282	0.19	80	353	1.0	19.6	16.7	8.6	7.9	0.0	0.0	0.7	33.9	2.7	0.7	1.3	2.2	2.4	0.0	0.0	6.5	45.3	11.6

Appendix 2: Experimental Data

Experiment CM D9

Start of Experiment: 19th August, 2003 at 10:30

Catalyst: H-MTW-100 (extrudates)

Si : Al ratio: 100

Pore Diameter (Å): 5.6 x 6.0

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g-m-cresol / g _{active catalyst} * h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D9-7	52	0.37	80	352	1.0	63.6	15.8	10.4	9.3	2.3	0.5	1.9	40.2	2.2	2.9	5.0	7.1	7.9	1.3	1.4	25.5	8.6	23.4
1	D9-8	56	0.37	80	352	1.0	62.7	15.6	10.5	9.6	2.1	0.5	1.8	40.1	2.1	2.9	4.7	7.1	7.6	1.3	1.3	24.9	9.2	23.7
1	D9-10	72	0.37	80	351	1.0	63.4	15.1	10.1	9.3	1.9	1.8	1.7	39.7	1.4	2.8	4.4	6.8	7.3	1.2	1.3	23.7	10.7	24.5
1	D9-11	81	0.37	80	354	1.0	61.9	14.6	10.2	9.7	1.6	1.8	1.5	39.3	1.3	2.7	4.0	6.6	6.8	1.0	1.2	22.2	12.4	24.8
1	D9-12	91	0.37	80	354	1.0	62.2	14.5	10.1	9.7	1.5	1.8	1.4	39.0	1.4	2.7	3.9	6.5	6.8	1.0	1.2	22.0	12.7	25.0
1		52-91	0.37	80	353	1.0	62.8	15.1	10.2	9.5	1.9	1.3	1.7	39.7	1.7	2.8	4.4	6.8	7.3	1.2	1.3	23.7	10.7	24.3
2	D9-16	141	0.19	80	355	1.0	70.8	15.9	9.2	8.1	2.3	0.7	1.8	37.9	2.7	3.0	5.0	7.3	8.4	1.4	1.5	26.6	7.3	25.5
2	D9-17	154	0.19	80	356	1.0	69.9	15.8	9.4	8.3	2.1	0.4	1.7	37.7	2.2	3.1	4.9	7.3	8.3	1.4	1.4	26.3	7.3	26.5
2	D9-18	165	0.19	80	355	1.0	69.1	15.7	9.3	8.4	2.0	0.5	1.7	37.6	2.2	3.0	4.7	7.2	8.0	1.3	1.3	25.5	8.3	26.3
2	D9-19	171	0.19	80	355	1.0	68.1	15.8	9.5	8.7	2.0	0.5	1.7	38.1	2.3	3.0	4.6	7.3	8.0	1.3	1.4	25.7	8.6	25.3
2		141-171	0.19	80	355	1.0	69.5	15.8	9.3	8.4	2.1	0.5	1.7	37.8	2.3	3.0	4.8	7.3	8.2	1.3	1.4	26.0	7.9	25.9
3	D9-24	189	0.93	80	353	1.0	48.5	11.2	10.6	12.1	0.7	1.2	1.1	37.0	1.1	1.5	1.9	4.3	4.3	0.4	0.8	13.2	26.4	22.4
3	D9-25	190	0.93	80	352	1.0	47.7	11.2	10.6	12.1	0.7	1.2	1.2	37.0	0.5	1.5	1.9	4.3	4.3	0.5	0.8	13.2	26.6	22.8
3	D9-26	193	0.93	80	353	1.0	47.4	11.2	10.6	12.2	0.7	1.2	1.1	37.0	0.5	1.4	1.8	4.2	4.2	0.4	0.8	12.8	27.6	22.1
3	D9-27	195	0.93	80	354	1.0	47.6	11.2	10.6	12.1	0.7	1.3	1.2	37.1	0.6	1.4	1.8	4.2	4.2	0.4	0.8	12.9	27.2	22.2
3		189-195	0.93	80	353	1.0	47.8	11.2	10.6	12.1	0.7	1.2	1.1	37.0	0.7	1.4	1.9	4.2	4.2	0.4	0.8	13.0	27.0	22.4

Appendix 2: Experimental Data

Experiment CM D10

Start of Experiment: 28th August, 2003 at 23:00

Catalyst: H-BEA-150 (powder)

Si : Al ratio: 150

Pore Diameter (Å): 5.6 x 5.6 <-> 6.6 x 6.7

Total Mass of Catalyst (g): 2.4 g

Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,6-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol Isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol Isomers	3-Methylanisole	"Others"
1	D10-13	119	0.37	80	354	1.0	63.5	14.4	11.2	10.5	2.7	1.1	5.4	45.3	3.6	5.0	6.1	4.7	6.5	3.2	1.5	26.9	0.7	23.5
1	D10-14	129	0.37	80	354	1.0	62.9	14.5	11.4	10.8	2.8	1.1	5.3	45.6	3.5	5.0	6.1	4.8	6.6	3.1	1.5	27.0	0.8	23.1
1	D10-15	137	0.37	80	354	1.0	62.0	14.7	11.6	11.2	2.5	1.0	5.1	46.2	3.4	4.9	6.0	4.8	6.6	3.0	1.5	26.8	0.9	22.8
1		120-138	0.37	80	354	1.0	62.8	14.6	11.4	10.8	2.6	1.1	5.3	45.7	3.5	5.0	6.1	4.8	6.5	3.1	1.5	26.9	0.8	23.1
2	D10-23	166	0.74	80	353	1.0	59.5	14.7	12.8	13.2	1.4	0.4	2.9	45.4	1.7	4.3	4.6	5.1	6.7	1.9	1.4	24.1	5.1	23.8
2	D10-24	169	0.74	80	354	1.0	59.7	14.7	13.0	13.3	1.3	0.4	2.7	45.4	1.4	4.3	4.7	5.2	6.8	1.8	1.5	24.2	5.3	23.7
2	D10-25	178	0.74	80	351	1.0	61.0	14.8	13.0	13.5	1.3	0.4	2.5	45.5	1.3	4.3	4.7	5.4	6.9	1.7	1.5	24.4	5.2	23.7
2		166-178	0.74	80	353	1.0	60.1	14.7	12.9	13.3	1.3	0.4	2.7	45.4	1.5	4.3	4.7	5.2	6.8	1.8	1.5	24.2	5.2	23.7
3	D10-31	203	1.49	80	352	1.0	52.9	14.5	11.8	12.9	0.5	0.6	0.5	40.7	1.1	1.4	2.1	3.9	4.3	0.2	0.9	12.8	24.9	20.4
3	D10-32	208	1.49	80	351	1.0	51.4	14.5	12.0	13.0	0.5	0.6	0.5	41.1	0.9	1.5	2.1	3.9	4.3	0.3	0.9	12.9	24.2	20.8
3		203-208	1.49	80	352	1.0	52.2	14.5	11.9	12.9	0.5	0.6	0.5	40.9	1.0	1.4	2.1	3.9	4.3	0.3	0.9	12.9	24.6	20.6
4	D10-36	279	0.37	80	352	1.0	59.3	15.0	13.2	14.0	0.9	0.2	1.7	45.0	0.9	3.5	3.9	5.5	6.7	1.1	1.4	22.0	8.3	23.8
4	D10-37	307	0.37	80	352	1.0	60.1	14.8	13.2	13.8	0.9	0.2	1.7	44.7	0.9	3.8	4.1	5.5	6.8	1.2	1.4	22.8	7.2	24.5
4		280-307	0.37	80	352	1.0	59.7	14.9	13.2	13.9	0.9	0.2	1.7	44.8	0.9	3.7	4.0	5.5	6.8	1.1	1.4	22.4	7.7	24.1

Appendix 2: Experimental Data

Experiment CM D11

Start of Experiment: 10th September, 2003 at 12:45

Catalyst: Siral (powder)

Si : Al ratio: 40 wt ratio

Pore Diameter (Å): N / A

Total Mass of Catalyst (g): 2.4 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol%)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} * h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D11-7	69	0.37	80	351	1.0	56.1	14.3	9.0	12.4	0.3	0.4	0.9	37.4	0.9	0.6	0.8	4.0	2.5	0.0	0.3	8.2	33.1	20.4
1	D11-8	79	0.37	80	350	1.0	55.6	14.0	9.0	12.4	0.3	0.4	0.9	36.9	0.7	0.5	0.7	3.8	2.4	0.0	0.3	7.9	33.9	20.6
1	D11-9	92	0.37	80	350	1.0	55.1	14.0	8.8	12.4	0.3	0.4	0.9	36.8	0.8	0.5	0.7	3.8	2.4	0.0	0.3	7.7	34.9	19.9
1		69-92	0.37	80	350	1.0	55.6	14.1	8.9	12.4	0.3	0.4	0.9	37.0	0.8	0.5	0.7	3.9	2.4	0.0	0.3	7.9	34.0	20.3
2	D11-14	146	0.19	80	353	1.0	61.9	17.0	10.4	12.7	0.6	0.4	1.1	42.2	1.4	1.4	1.7	6.1	4.8	0.4	0.6	15.0	14.5	26.9
2	D11-15	153	0.19	80	353	1.0	63.1	17.3	10.3	12.5	0.6	0.4	1.0	42.1	1.2	1.5	1.8	6.3	5.0	0.3	0.7	15.5	13.7	27.5
2	D11-16	163	0.19	80	351	1.0	62.3	18.0	10.4	12.7	0.7	0.4	1.0	43.2	1.2	1.4	1.8	6.4	5.1	0.3	0.6	15.6	15.3	24.6
2		146-164	0.19	80	352	1.0	62.5	17.4	10.4	12.6	0.6	0.4	1.1	42.5	1.3	1.5	1.8	6.2	5.0	0.3	0.7	15.4	14.5	26.3
3	D11-18	172	0.74	80	351	1.0	48.6	11.0	6.8	10.2	0.2	0.4	0.4	29.0	0.1	1.6	0.3	1.9	1.1	0.0	0.2	5.1	53.0	12.8
3	D11-19	178	0.74	80	352	1.0	49.7	11.0	6.8	10.2	0.2	0.5	0.5	29.2	0.6	0.2	0.4	2.0	1.2	0.0	0.2	3.8	53.2	13.1
3	D11-20	180	0.74	80	352	1.0	49.3	11.4	7.1	10.5	0.2	0.5	0.5	30.2	0.2	0.2	0.4	2.1	1.2	0.0	0.2	4.1	51.6	13.9
3	D11-21	187	0.74	80	351	1.0	49.9	10.7	6.6	10.0	0.2	0.4	0.5	28.4	0.2	0.2	0.3	1.9	1.1	0.0	0.1	3.6	54.8	13.0
3	D11-22	190	0.74	80	348	1.0	49.2	10.6	6.5	9.9	0.2	0.5	0.5	28.2	0.2	0.2	0.3	1.8	1.0	0.0	0.1	3.5	55.0	13.2
3	D11-23	194	0.74	80	351	1.0	49.8	10.6	6.5	9.9	0.2	0.4	0.5	28.0	0.6	0.2	0.3	1.8	1.1	0.0	0.2	3.6	55.1	12.7
3	D11-24	196	0.74	80	352	1.0	48.4	11.4	7.0	10.7	0.2	0.6	0.5	30.4	0.4	0.2	0.4	2.0	1.2	0.0	0.2	3.9	51.4	13.9
3		172-196	0.74	80	351	1.0	49.3	11.0	6.7	10.2	0.2	0.5	0.5	29.1	0.3	0.4	0.3	1.9	1.1	0.0	0.2	3.9	53.4	13.2
4	D11-28	210	1.49	80	351	1.0	41.3	9.5	5.2	8.1	0.2	1.0	0.2	24.2	0.0	0.0	0.2	0.9	0.5	0.0	0.1	1.6	65.0	8.6
4	D11-29	214	1.49	80	352	1.0	42.3	8.8	5.3	8.3	0.0	0.0	0.0	22.3	0.0	0.0	0.0	0.9	0.5	0.0	0.0	1.4	68.1	8.2
4	D11-30	217	1.49	80	352	1.0	41.6	8.8	5.6	8.5	0.2	0.6	0.2	23.9	0.0	0.0	0.2	0.9	0.5	0.0	0.1	1.7	65.6	9.0
4	D11-31	219	1.49	80	352	1.0	40.8	9.1	5.5	8.6	0.0	0.6	0.2	24.0	0.0	0.0	0.0	0.9	0.5	0.0	0.0	1.4	66.0	8.6
4	D11-32	220	1.49	80	352	1.0	42.0	8.6	5.3	8.2	0.0	0.5	0.2	22.8	0.0	0.0	0.2	0.9	0.5	0.0	0.0	1.5	68.2	8.1
4		210-220	1.49	80	352	1.0	41.6	9.0	5.4	8.3	0.1	0.5	0.2	23.5	0.0	0.0	0.1	0.9	0.5	0.0	0.0	1.5	66.6	8.5

Appendix 2: Experimental Data

Experiment CM D12

Start of Experiment: 1st October, 2002 at 11:15

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} • h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	p- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
1	D12-9	105	0.37	80	354	1.0	59.5	17.7	12.4	4.4	0.6	1.6	9.8	46.4	9.4	0.5	0.4	3.3	15.3	0.9	0.2	20.6	1.8	21.7
1	D12-10	116	0.37	80	354	1.0	58.8	17.5	12.6	4.4	0.7	1.5	9.3	45.9	9.0	0.5	0.4	3.1	14.8	0.8	0.2	19.8	2.3	23.1
1	D12-11	122	0.37	80	354	1.0	56.9	17.9	13.2	4.5	0.6	1.4	9.2	46.8	8.4	0.5	0.4	3.0	14.6	0.8	0.3	19.6	2.4	22.8
1	105-130		0.37	80	354	1.0	58.4	17.7	12.7	4.4	0.6	1.5	9.4	46.4	8.9	0.5	0.4	3.1	14.9	0.8	0.2	20.0	2.2	22.5
2	D12-15	143	0.37	80	304	1.0	24.0	15.0	17.1	11.8	0.0	0.0	0.3	44.3	0.2	0.3	2.5	1.4	2.3	0.0	0.0	6.5	31.5	17.4
2	D12-16	146	0.37	80	305	1.0	24.1	14.4	16.0	11.9	0.0	0.0	0.0	42.2	0.2	0.3	2.1	1.3	1.8	0.0	0.0	5.5	35.2	16.9
2	D12-17	154	0.37	80	305	1.0	24.3	14.1	15.6	12.0	0.0	0.0	0.0	41.7	0.8	0.3	2.0	1.2	1.7	0.0	0.0	5.2	37.3	15.1
2	D12-18	163	0.37	80	305	1.0	24.2	13.9	15.3	12.0	0.0	0.0	0.0	41.1	0.7	0.3	1.8	1.2	1.6	0.0	0.0	4.9	38.4	14.9
2	D12-19	165	0.37	80	305	1.0	24.3	13.7	15.0	11.8	0.0	0.0	0.0	40.5	1.3	0.3	0.3	1.2	1.5	0.0	0.0	3.4	38.5	16.3
2	142-165		0.37	80	305	1.0	24.2	14.2	15.8	11.9	0.0	0.0	0.1	42.0	0.6	0.3	1.8	1.3	1.8	0.0	0.0	5.1	36.2	16.1
3	D12-22	171	0.74	80	306	1.0	15.4	13.5	14.7	11.9	0.0	0.0	0.0	40.1	0.4	0.0	1.3	0.9	1.1	0.0	0.0	3.4	46.8	9.4
3	D12-23	173	0.74	80	306	1.0	15.4	13.1	14.3	11.7	0.0	0.0	0.0	39.1	0.4	0.0	1.3	0.9	1.1	0.0	0.0	3.3	47.9	9.3
3	D12-24	177	0.74	80	306	1.0	15.7	12.8	14.1	11.4	0.0	0.0	0.0	38.3	2.6	0.0	1.3	0.8	1.1	0.0	0.0	3.2	46.6	9.3
3	D12-25	179	0.74	80	306	1.0	15.1	13.0	14.5	11.8	0.0	0.0	0.0	39.3	0.5	0.0	1.3	0.9	1.0	0.0	0.0	3.2	48.4	8.6
3	171-179		0.74	80	306	1.0	15.4	13.1	14.4	11.7	0.0	0.0	0.0	39.2	1.0	0.0	1.3	0.9	1.1	0.0	0.0	3.3	47.4	9.1
4	D12-28	189	1.49	80	306	1.0	8.7	12.4	13.4	11.2	0.0	0.0	0.0	37.0	0.9	0.0	0.0	0.0	0.7	0.0	0.0	0.7	55.5	5.8
4	D12-29	191	1.49	80	306	1.0	8.8	12.1	13.2	11.0	0.0	0.0	0.0	36.3	0.8	0.0	0.8	0.0	0.8	0.0	0.0	1.6	54.6	6.8
4	D12-30	192	1.49	80	306	1.0	8.7	12.2	13.2	11.1	0.0	0.0	0.0	36.5	0.8	0.0	0.7	0.0	0.8	0.0	0.0	1.5	55.3	5.9
4	189-192		1.49	80	306	1.0	8.8	12.2	13.2	11.1	0.0	0.0	0.0	36.6	0.8	0.0	0.5	0.0	0.8	0.0	0.0	1.3	55.2	6.2
5	D12-33	195	2.97	80	306	1.0	4.6	11.8	13.1	11.0	0.0	0.0	0.0	35.9	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.5	5.4
5	D12-34	196	2.97	80	305	1.0	4.8	11.1	11.6	10.2	0.0	0.0	0.0	32.9	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	63.8	1.5
5	D12-35	197	2.97	80	306	1.0	5.0	11.0	11.7	10.0	0.0	0.0	0.0	32.7	6.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	57.5	3.4
5	195-197		2.97	80	306	1.0	4.8	11.3	12.1	10.4	0.0	0.0	0.0	33.8	3.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	59.3	3.4
6	D12-38	198	3.45	80	306	0.5	4.4	11.4	12.1	10.4	0.0	0.0	0.0	34.0	3.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	59.5	3.1
6	D12-39	199	3.45	80	306	0.5	4.4	11.4	12.3	10.7	0.0	0.0	0.0	34.4	5.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	59.1	0.9
6	D12-40	199	3.45	80	306	0.5	4.4	11.2	11.9	10.3	0.0	0.0	0.0	33.4	5.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.0	0.9
6	198-199		3.45	80	306	0.5	4.4	11.4	12.1	10.5	0.0	0.0	0.0	33.9	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	59.5	1.6
7	D12-44	217	0.86	80	306	0.5	12.1	12.6	13.9	11.4	0.0	0.0	0.0	38.0	1.9	0.0	1.3	0.8	1.1	0.0	0.0	3.1	50.3	6.8
7	D12-45	220	0.86	80	306	0.5	12.1	12.5	13.6	11.3	0.0	0.0	0.0	37.3	2.0	0.0	1.2	0.8	1.0	0.0	0.0	3.0	50.9	6.9
7	D12-46	222	0.86	80	306	0.5	12.1	12.4	13.7	11.3	0.0	0.0	0.0	37.4	2.9	0.0	1.2	0.7	1.0	0.0	0.0	2.9	50.0	6.8
7	217-222		0.86	80	306	0.5	12.1	12.5	13.7	11.3	0.0	0.0	0.0	37.6	2.2	0.0	1.2	0.8	1.0	0.0	0.0	3.0	50.4	6.8

Appendix 2: Experimental Data

Experiment CM D12 (continued)

Start of Experiment: 1st October, 2002 at 11:15

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g

Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,6-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
8	D12-49	268	0.43	80	305	0.5	18.5	13.7	15.2	12.2	0.0	0.0	0.0	41.1	1.2	0.0	1.4	0.9	1.4	0.0	0.0	3.7	43.6	10.4
8	D12-50	276	0.43	80	306	0.5	18.7	13.7	15.2	12.3	0.0	0.0	0.0	41.2	1.1	0.0	1.4	1.0	1.4	0.0	0.0	3.8	43.5	10.4
8	D12-51	285	0.43	80	306	0.5	18.7	13.6	15.2	12.1	0.0	0.0	0.0	40.9	1.2	0.0	1.4	0.9	1.4	0.0	0.0	3.7	43.2	10.9
8	D12-52	290	0.43	80	306	0.5	18.7	13.6	15.0	12.0	0.0	0.0	0.0	40.6	1.1	0.0	1.4	0.9	1.3	0.0	0.0	3.7	43.5	11.1
8		268-290	0.43	80	306	0.5	18.7	13.6	15.2	12.1	0.0	0.0	0.0	40.9	1.2	0.0	1.4	0.9	1.4	0.0	0.0	3.7	43.5	10.7
9	D12-56	297	1.73	80	306	0.5	8.0	11.2	12.0	10.2	0.0	0.0	0.0	33.4	7.4	0.0	0.8	0.0	0.8	0.0	0.0	1.6	53.6	3.9
9	D12-57	297	1.73	80	306	0.5	7.8	11.3	12.0	10.4	0.0	0.0	0.0	33.7	6.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.3	3.8
9		297-298	1.73	80	306	0.5	7.9	11.2	12.0	10.3	0.0	0.0	0.0	33.6	6.8	0.0	0.4	0.0	0.4	0.0	0.0	0.8	55.0	3.9
10	D12-61	313	0.58	80	306	2.0	16.4	12.8	14.1	11.8	0.0	0.0	0.0	38.6	1.5	0.0	0.7	0.8	0.9	0.0	0.0	2.5	49.7	7.7
10	D12-62	314	0.58	80	305	2.0	16.6	12.7	13.8	11.6	0.0	0.0	0.0	38.0	1.4	0.0	0.7	0.8	0.9	0.0	0.0	2.4	50.5	7.7
10	D12-63	315	0.58	80	305	2.0	16.5	12.8	13.8	11.6	0.0	0.0	0.0	38.2	1.4	0.0	0.7	0.8	0.9	0.0	0.0	2.4	50.1	7.9
10		313-315	0.58	80	305	2.0	16.5	12.8	13.9	11.6	0.0	0.0	0.0	38.3	1.4	0.0	0.7	0.8	0.9	0.0	0.0	2.4	50.1	7.8
11	D12-67	318	1.16	80	305	2.0	9.7	12.0	13.0	11.0	0.0	0.0	0.0	36.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.8	4.7
11	D12-68	318	1.16	80	305	2.0	9.6	12.0	13.0	10.9	0.0	0.0	0.0	35.9	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.8	4.8
11	D12-69	321	1.16	80	304	2.0	9.4	11.9	13.0	11.1	0.0	0.0	0.0	35.9	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.9	4.6
11		318-321	1.16	80	305	2.0	9.6	12.0	13.0	11.0	0.0	0.0	0.0	35.9	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	56.8	4.7
12	D12-72	322	2.33	80	304	2.0	5.1	11.0	11.7	10.0	0.0	0.0	0.0	32.7	5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	61.2	1.0
12	D12-73	323	2.33	80	304	2.0	5.4	10.5	11.0	9.2	0.0	0.0	0.0	30.6	6.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	58.1	5.1
12	D12-74	324	2.33	80	304	2.0	5.1	10.9	11.4	10.0	0.0	0.0	0.0	32.3	5.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	61.4	1.1
12		322-324	2.33	80	304	2.0	5.2	10.8	11.4	9.7	0.0	0.0	0.0	31.9	5.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.2	2.4
13	D12-78	357	0.29	80	301	2.0	24.4	12.7	13.7	11.7	0.0	0.0	0.0	38.0	0.8	0.4	0.9	1.1	1.1	0.0	0.0	3.6	44.1	13.5
13	D12-79	361	0.29	80	301	2.0	23.8	12.9	13.8	11.9	0.0	0.0	0.0	38.7	1.1	0.3	1.0	1.1	1.2	0.0	0.0	3.5	42.6	14.1
13	D12-80	368	0.29	80	302	2.0	24.1	12.6	13.5	11.6	0.0	0.0	0.0	37.7	0.9	0.0	0.9	1.1	1.1	0.0	0.0	3.1	45.4	12.8
13		357-368	0.29	80	301	2.0	24.1	12.7	13.7	11.7	0.0	0.0	0.0	38.1	1.0	0.2	0.9	1.1	1.1	0.0	0.0	3.4	44.0	13.5
14	D12-85	430	0.15	80	301	2.0	33.3	15.6	16.6	12.5	0.0	0.0	0.2	44.9	1.1	0.5	0.3	2.2	2.8	0.0	0.1	5.9	22.9	25.3
14	D12-86	440	0.15	80	301	2.0	35.1	14.3	14.7	11.2	0.0	0.0	0.0	40.2	1.3	0.4	1.3	2.0	2.5	0.0	0.0	6.2	28.4	24.0
14		430-440	0.15	80	301	2.0	34.2	14.9	15.6	11.9	0.0	0.0	0.1	42.5	1.2	0.5	0.8	2.1	2.6	0.0	0.1	6.0	25.6	24.6

Appendix 2: Experimental Data

Experiment CM D12 (continued)

Start of Experiment: 1st October, 2002 at 11:15

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 3.0 g Mass of Active Catalyst (g): 2.4 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} • h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol Isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
15	D12-90	487	0.19	80	303	1.0	31.6	13.7	14.3	11.9	0.0	0.0	0.0	40.0	0.5	0.4	1.5	1.6	1.9	0.0	0.2	5.6	35.5	18.5
15	D12-91	502	0.19	80	303	1.0	31.0	14.5	15.8	12.7	0.0	0.0	0.0	43.0	0.1	0.4	1.7	1.8	2.1	0.0	0.3	6.2	31.7	19.0
15	D12-92	512	0.19	80	303	1.0	31.9	13.9	15.0	12.2	0.0	0.0	0.0	41.0	0.1	0.4	1.6	1.6	2.0	0.0	0.3	6.0	33.2	19.7
15	D12-93	525	0.19	80	303	1.0	31.9	13.7	14.4	12.0	0.0	0.0	0.0	40.2	0.1	0.3	1.5	1.6	1.9	0.0	0.2	5.6	35.1	19.0
15	D12-94	537	0.19	80	303	1.0	31.5	13.9	14.6	12.1	0.0	0.0	0.0	40.6	0.1	0.4	1.5	1.6	1.9	0.0	0.0	5.4	35.2	18.8
15	D12-95	547	0.19	80	303	1.0	31.6	14.1	15.6	12.5	0.1	0.0	0.2	42.5	0.1	0.4	1.7	1.7	2.1	0.0	0.3	6.1	31.1	20.1
15	487-547		0.19	80	303	1.0	31.6	14.0	15.0	12.2	0.0	0.0	0.0	41.2	0.1	0.4	1.6	1.7	2.0	0.0	0.2	5.8	33.6	19.2
16	D12-100	622	0.22	80	306	0.5	29.0	15.0	17.8	13.4	0.0	0.0	0.3	46.5	0.2	0.3	1.6	1.4	2.2	0.0	0.3	5.8	28.8	18.8
16	D12-101	630	0.22	80	306	0.5	28.3	14.9	17.3	13.1	0.2	0.0	0.4	45.9	0.5	0.3	1.6	1.4	2.0	0.0	0.1	5.4	32.3	15.9
16	D12-102	645	0.22	80	306	0.5	28.8	14.8	16.9	13.0	0.0	0.0	0.4	45.1	0.2	0.3	1.6	1.3	2.1	0.0	0.3	5.5	31.0	18.2
16	622-645		0.22	80	306	0.5	28.7	14.9	17.3	13.2	0.1	0.0	0.4	45.8	0.3	0.3	1.6	1.4	2.1	0.0	0.2	5.6	30.7	17.6
17	D12-105	675	0.43	80	306	0.5	18.9	13.6	15.1	12.4	0.0	0.0	0.0	41.2	0.4	0.0	1.3	0.9	1.3	0.0	0.0	3.6	44.7	10.2
17	D12-107	701	0.43	80	306	0.5	18.5	13.7	15.6	12.6	0.0	0.0	0.0	41.9	0.4	0.0	1.3	0.9	1.3	0.0	0.0	3.6	44.9	9.2
17	D12-108	716	0.43	80	306	0.5	18.7	13.9	16.1	12.9	0.0	0.0	0.0	42.9	0.5	0.0	1.3	1.0	1.4	0.0	0.0	3.7	42.8	10.0
17	675-692		0.43	80	306	0.5	18.9	13.6	15.1	12.4	0.0	0.0	0.0	41.2	0.4	0.0	1.3	0.9	1.3	0.0	0.0	3.6	44.7	10.2
18	D12-110	741	0.43	80	326	0.5	27.7	16.4	18.6	12.8	0.2	0.2	0.8	48.9	1.4	0.4	0.2	1.7	3.0	0.0	0.3	5.7	25.7	18.3
18	D12-111	752	0.43	80	326	0.5	27.6	16.7	18.6	12.8	0.0	0.0	0.8	48.9	0.9	0.4	1.6	1.7	3.1	0.0	0.3	7.1	26.5	16.7
18	D12-112	768	0.43	80	326	0.5	27.7	16.5	18.2	12.6	0.0	0.0	0.8	48.1	0.8	0.4	1.6	1.7	3.1	0.0	0.3	7.0	26.4	17.7
18	741-768		0.43	80	326	0.5	27.7	16.5	18.5	12.7	0.1	0.1	0.8	48.7	1.0	0.4	1.1	1.7	3.1	0.0	0.3	6.6	26.2	17.6

Appendix 2: Experimental Data

Experiment CM D13

Start of Experiment: 27th November, 2003 at 15:10

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 12.0 g Mass of Active Catalyst (g): 9.6 g

Sample Information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol Isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol Isomers	3-Methylanisole	"Others"
1	D13-3	47	0.09	80	301	1.0	52.2	16.9	14.3	5.6	0.8	0.8	8.2	46.8	13.4	0.2	0.3	1.4	6.7	0.0	0.3	8.8	0.6	30.4
1	D13-4	54	0.09	80	302	1.0	51.8	17.3	15.2	5.7	0.4	0.8	8.0	47.5	12.5	0.3	0.3	1.3	7.2	0.2	0.3	9.5	0.3	30.3
1		47-54	0.09	80	302	1.0	52.0	17.1	14.8	5.6	0.6	0.8	8.1	47.1	12.9	0.2	0.3	1.3	7.0	0.1	0.3	9.2	0.4	30.3
2	D13-9	94	0.19	80	302	1.0	45.3	19.1	21.9	7.8	0.2	0.2	3.6	52.8	1.7	0.2	2.8	1.4	6.9	0.0	0.2	11.7	6.9	27.0
2	D13-10	105	0.19	80	302	1.0	44.6	18.2	21.6	8.3	0.0	0.0	2.3	50.4	0.8	0.2	3.4	1.4	5.7	0.0	0.2	11.0	9.7	28.1
2	D13-11	115	0.19	80	302	1.0	44.1	17.4	20.6	8.9	0.0	0.0	1.5	48.3	0.6	0.5	3.4	1.5	4.7	0.0	0.7	10.8	13.3	27.0
2		94-115	0.19	80	302	1.0	44.7	18.2	21.3	8.3	0.1	0.1	2.4	50.5	1.1	0.3	3.2	1.5	5.8	0.0	0.4	11.1	10.0	27.3
3	D13-15	125	0.37	80	303	1.0	32.7	13.6	15.4	9.9	0.0	0.0	0.4	39.3	0.1	0.2	2.0	1.0	2.0	0.0	0.4	5.7	36.0	18.9
3	D13-16	128	0.37	80	303	1.0	32.2	12.8	14.6	10.0	0.0	0.0	0.0	37.5	0.1	0.3	1.9	1.0	1.6	0.0	0.3	5.1	40.4	16.9
3	D13-17	136	0.37	80	303	1.0	32.2	12.5	13.7	10.1	0.0	0.0	0.0	36.3	0.0	0.3	1.7	0.9	1.4	0.0	0.3	4.6	43.5	15.5
3	D13-18	138	0.37	80	303	1.0	32.1	12.5	13.6	10.2	0.0	0.0	0.0	36.3	0.0	0.3	1.6	0.9	1.3	0.0	0.3	4.5	44.8	14.4
3		125-138	0.37	80	303	1.0	32.3	12.9	14.3	10.1	0.0	0.0	0.1	37.4	0.1	0.3	1.8	1.0	1.6	0.0	0.3	5.0	41.2	16.4
4	D13-21	141	0.74	80	303	1.0	21.4	11.5	12.6	9.9	0.0	0.0	0.0	34.0	0.2	0.0	1.0	0.6	0.9	0.0	0.0	2.5	55.8	7.5
4	D13-22	141	0.74	80	303	1.0	21.9	11.4	12.4	9.9	0.0	0.0	0.0	33.7	0.1	1.0	0.0	0.6	0.9	0.0	0.0	2.5	55.4	8.3
4	D13-23	144	0.74	80	303	1.0	22.5	11.2	12.0	9.6	0.0	0.0	0.0	32.8	0.1	1.0	0.0	0.6	0.8	0.0	0.0	2.4	57.1	7.6
4		141-144	0.74	80	303	1.0	21.9	11.4	12.3	9.8	0.0	0.0	0.0	33.5	0.1	0.7	0.3	0.6	0.9	0.0	0.0	2.4	56.1	7.8
5	D13-25	145	1.49	80	303	1.0	14.8	10.0	10.7	8.8	0.0	0.0	0.0	29.5	2.2	0.5	0.0	0.0	0.6	0.0	0.0	1.1	63.4	3.9
5	D13-26	146	1.49	80	303	1.0	14.8	10.0	10.6	8.9	0.0	0.0	0.0	29.5	0.4	0.5	0.0	0.0	0.5	0.0	0.0	1.1	64.0	5.1
5	D13-27	146	1.49	80	303	1.0	14.5	10.0	10.8	9.0	0.0	0.0	0.0	29.8	0.4	0.0	0.0	0.0	0.5	0.0	0.0	0.5	64.9	4.4
5		145-146	1.49	80	303	1.0	14.7	10.0	10.7	8.9	0.0	0.0	0.0	29.6	1.0	0.3	0.0	0.0	0.6	0.0	0.0	0.9	64.1	4.5
6	D13-31	213	0.05	80	308	1.0	60.9	19.2	18.0	10.2	0.4	0.4	3.0	51.1	2.0	0.4	0.5	3.9	8.0	0.0	0.3	13.1	2.1	31.7
6	D13-32	257	0.05	80	311	1.0	62.5	19.1	16.3	9.0	0.3	0.5	4.0	49.2	2.1	0.4	0.5	4.1	9.1	0.0	0.2	14.2	2.0	32.5
6	D13-33	267	0.05	80	309	1.0	61.3	19.8	16.5	8.9	0.4	0.5	4.5	50.6	3.1	0.5	0.5	4.1	9.9	0.0	0.2	15.1	1.8	29.5
6	D13-34	281	0.05	80	307	1.0	61.3	19.2	16.4	8.6	0.3	0.5	4.2	49.3	2.4	0.4	0.4	4.0	9.6	0.0	0.2	14.6	2.0	31.7
6	D13-35	292	0.05	80	305	1.0	60.7	19.3	16.8	8.8	0.3	0.5	4.1	49.8	2.4	0.4	0.4	3.7	8.8	0.0	0.2	13.6	2.1	32.2
6		213-292	0.05	80	308	1.0	61.4	19.3	16.8	9.1	0.3	0.5	3.9	50.0	2.4	0.4	0.5	4.0	9.1	0.0	0.2	14.1	2.0	31.5

Appendix 2: Experimental Data

Experiment CM D13 (continued)

Start of Experiment: 27th November, 2003 at 15:10

Catalyst: H-MFI-90 (extrudates)

Si : Al ratio: 90

Pore Diameter (Å): 5.1 x 5.5 <-> 5.3 x 5.6

Total Mass of Catalyst (g): 12.0 g Mass of Active Catalyst: 9.6 g

Sample information			Operating parameters				Selectivities (mol %)																	
Setting Number	Sample Reference	Time on Stream	WHSV (g _{m-cresol} / g _{active catalyst} · h)	Pressure (bar)	Cat Bed Temperature (°C)	Methanol : m-cresol (molar ratio)	Conversion (%)	2,5-Xylenol	3,4-Xylenol	2,3-Xylenol	3,5-Xylenol	2,6-Xylenol	2,4-Xylenol	Total Xylenol isomers	o- & p-Cresol	2,3,4-Trimethylphenol	2,3,5-Trimethylphenol	2,3,6-Trimethylphenol	2,4,5-Trimethylphenol	2,4,6-Trimethylphenol	3,4,5-Trimethylphenol	Total Trimethylphenol isomers	3-Methylanisole	"Others"
7	D13-43	393	0.09	80	303	1.0	52.2	17.4	20.2	11.3	0.0	0.5	1.0	50.3	0.2	0.4	3.2	2.4	4.5	0.0	0.2	10.6	11.2	27.5
7	D13-44	415	0.09	80	303	1.0	52.2	17.3	19.9	11.4	0.0	0.5	0.9	50.0	0.1	0.4	3.2	2.3	4.4	0.0	0.2	10.5	12.0	27.4
7	D13-45	426	0.09	80	302	1.0	52.2	17.1	19.9	11.4	0.0	0.5	0.8	49.7	0.0	0.4	3.2	2.3	4.3	0.0	0.2	10.3	12.5	27.4
7	D13-46	434	0.09	80	302	1.0	52.0	17.0	19.6	11.4	0.0	0.5	0.8	49.4	0.1	0.4	3.2	2.3	4.2	0.0	0.2	10.2	13.1	27.1
7	D13-47	463	0.09	80	303	1.0	51.9	17.2	19.7	11.6	0.0	0.5	0.8	49.7	0.0	0.4	3.2	2.3	4.3	0.0	0.3	10.3	13.4	26.6
7	D13-48	481	0.09	80	303	1.0	52.4	16.8	19.3	11.4	0.0	0.5	0.7	48.8	0.1	0.3	3.1	2.3	4.1	0.0	0.3	10.2	13.5	27.4
7	D13-49	499	0.09	80	302	1.0	52.2	16.5	19.2	11.4	0.0	0.5	0.7	48.2	0.1	0.3	3.1	2.2	4.0	0.0	0.3	10.0	14.1	27.6
7	D13-50	506	0.09	80	303	1.0	51.8	16.5	19.0	11.4	0.0	0.4	0.7	48.0	0.1	0.3	3.0	2.3	3.9	0.0	0.3	9.9	14.8	27.2
7	393-506		0.09	80	303	1.0	52.1	17.0	19.6	11.4	0.0	0.5	0.8	49.3	0.1	0.3	3.1	2.3	4.2	0.0	0.3	10.3	13.1	27.3
8	D13-56	652	0.09	30	303	1.0	44.6	13.3	13.2	10.0	0.0	0.5	0.2	37.3	0.1	0.2	1.8	1.3	2.1	0.0	0.2	5.7	38.0	18.9
8	D13-57	678	0.09	30	303	1.0	43.4	14.0	13.8	10.5	0.2	0.5	0.3	39.3	0.1	0.2	1.8	1.5	2.1	0.0	0.2	5.9	35.4	19.4
8	D13-58	723	0.09	30	303	1.0	44.5	13.3	13.1	10.1	0.0	0.5	0.2	37.2	0.1	0.2	1.7	1.4	2.0	0.0	0.2	5.5	38.7	18.5
8	D13-59	727	0.09	30	303	1.0	41.3	15.1	15.2	11.5	0.0	0.7	0.4	43.0	0.6	0.3	2.0	1.5	2.4	0.0	0.3	6.4	31.2	18.8
8	D13-60	755	0.09	30	303	1.0	43.8	13.7	13.4	10.4	0.0	0.5	0.3	38.2	0.0	0.2	1.7	1.4	2.1	0.0	0.2	5.7	37.6	18.5
8	D13-61	760	0.09	30	303	1.0	41.2	15.3	15.5	11.8	0.2	0.7	0.3	43.9	0.6	0.3	2.0	1.6	2.4	0.0	0.2	6.6	29.6	19.3
8	652-760		0.09	30	303	1.0	43.1	14.1	14.0	10.7	0.1	0.6	0.3	39.8	0.2	0.2	1.8	1.5	2.2	0.0	0.2	6.0	35.1	18.9

Appendix 3: Calibration of the Mass Flow Controller

Mass Flow Controllers must be calibrated so that the amount of gas flowing through at any time can be determined. The mass flow controller is gauged on a percentage basis, with 100 % representing sensor capacity fully used. The calibration is conducted to determine the amount of gas flowing through for any given percentage indicated. Theoretically a straight line through the origin should result with the percentage indicated reflecting precisely the percentage of Mass Flow Controller capacity. However, in practice this is not exactly so. Usually a linear relationship is obtained between 5 % and 95 % indication, deviating slightly from the origin and the theoretical slope.

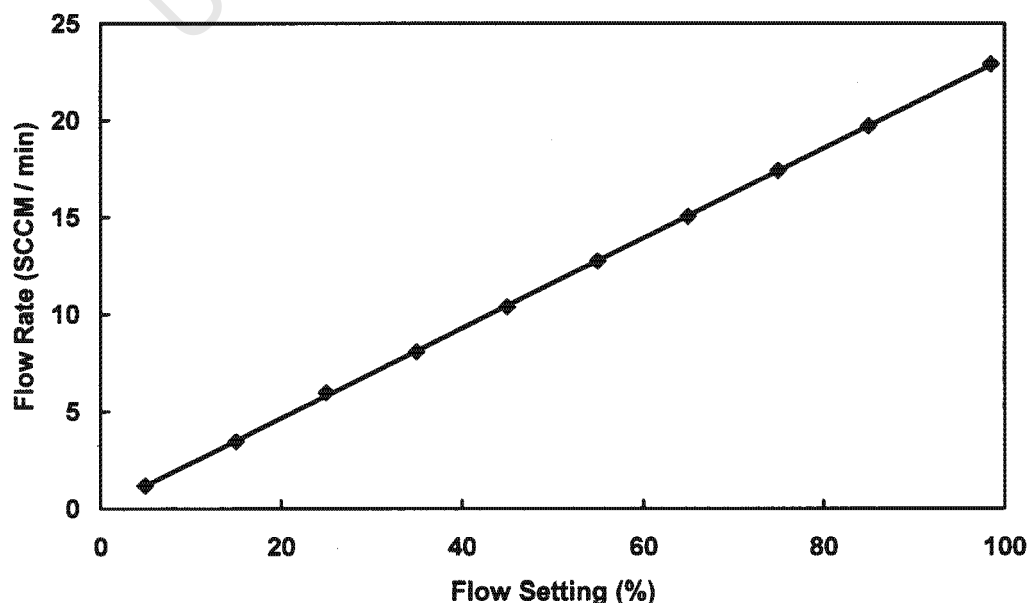
For the Mass Flow Controller used, maximum operating pressure was 35 bar. The pressure difference over the mass flow controller was controlled at less than 5 bar (as per design specifications).

The calibration is done as follows:

- Choose a set point (%)
- Measure the volume of air flow per unit time (done by repeatedly timing the movement of a bubble in a bubble flow meter)

The following calibration line was determined after performing gas flow tests at 25°C and 1.01 bar. The trend line provides the following relationship between set point and gas flow rate:

$$\text{Flow (SCCM / min)} = 0.232 \cdot \text{set point (\%)} + 0.014$$



Appendix 4: Identifying Peaks of 2,3,4-trimethylphenol and 2,4,5-trimethylphenol in Gas Chromatogram

Pure samples for many of the product compounds were obtained, which enabled identification of most major peaks in the product chromatograms. Portions of a product samples were spiked with small amounts of these pure samples and then injected into the Gas Chromatograph (GC) in order to identify the peaks representing each of these compounds in the product.

However, it was not possible to source pure samples for all relevant products. In particular, it was not possible to source each and every trimethylphenol isomer. Only pure compounds of isomers 2,3,5-, 2,3,6-, 2,4,6- and 3,4,5-trimethylphenol were commercially available. Analysis of a mixture of the four available out of six possible trimethylphenol isomers showed two additional fairly prominent but unknown peaks that were ascribed to the missing trimethylphenols. Thus in order to distinguish these peaks for 2,4,5- and 2,3,4-trimethylphenol, it was necessary to determine the relative probability of these two isomers forming (see figure A4-1).

Figure A4-1 shows the reaction pathways in the *m*-cresol methylation system, firstly through primary methylation to xylenols and then, via secondary methylation, to trimethylphenols.

Thus, the largest of the two peaks of individually unidentified trimethylphenols forming represents 2,4,5-trimethylphenol. The other represents 2,3,4-trimethylphenol.

However, no clear evidence was found for any shape selective restrictions or preferences being effected on the trimethylphenols by the zeolite catalyst. So only the sum of the trimethylphenols is given in the results.

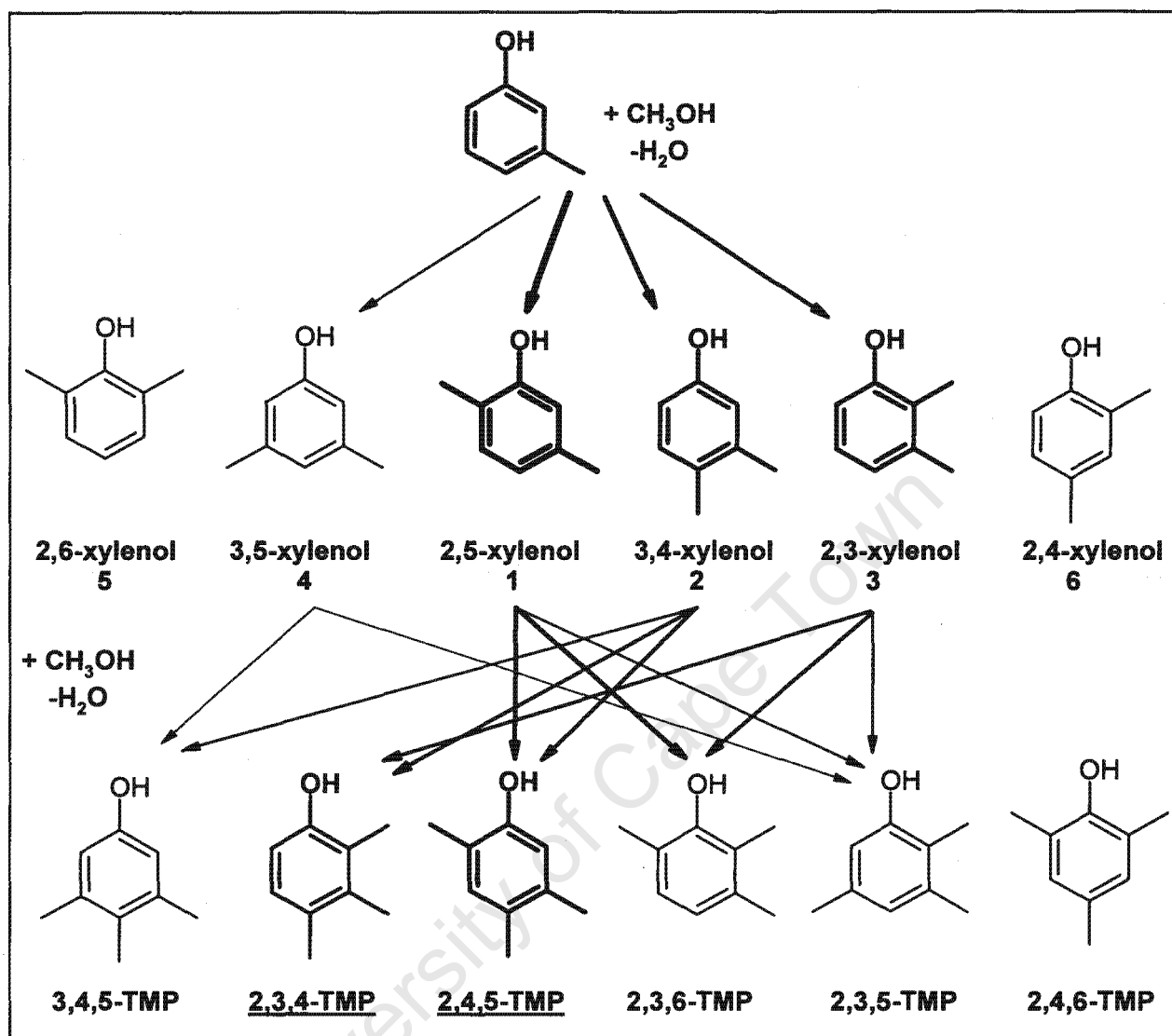


Figure A4-1: Routes towards formation of trimethylphenols via methylation of first *m*-cresol and then methylation of the xyleneol primary products. Routes from secondary xyleneol products, i.e. those that only form via additional 1,2-shift isomerisation, are not shown. Kinetic reaction paths to the two trimethylphenols (2,4,5- and 2,3,4-trimethylphenol, underlined) whose peaks had to be distinguished, give an indication of their relative prevalence in the reaction product. Reaction pathways and prevalence of precursors (2,5-xyleneol) indicate towards formation 2,4,5-trimethylphenol isomer with preference over the 2,3,4-trimethylphenol isomer.

Appendix 5: Calculation of Reaction Order and Activation Energy

1. Determination of reaction order

Find symbols used in this section in the symbols index.

1.1 Zero order reaction

In a zero order reaction the rate law is as shown in equation A5-1.

Equation A5-1: Rate law for a zero order reaction (Fogler, 1999)

$$-r_A = k_A$$

For a packed bed reactor (PBR), the integral relationship between rate of reaction and mass of catalyst is given in equation A5-2.

Equation A5-2: Design equation for a packed bed reactor (Fogler, 1999)

$$W = F_A^o \cdot \int_0^X \frac{dX}{-r_A}$$

Equations A5-3 to A5-5 detail the procedure towards deriving a relationship between WHSV and conversion.

Equation A5-3: Design equation for a zero order reaction (Fogler, 1999)

$$\frac{W}{F_A^o} = \int_0^X \frac{dX}{k_A} = \frac{1}{k_A} \cdot X$$

Equation A5-4: Relationship of mass of catalyst and flow rate with space velocity (derived from Fogler, 1999)

$$\frac{W}{F_A^o} = \tau = \frac{1}{WHSV}$$

Equation A5-5: Relationship between space velocity and conversion for a zero order reaction (derived from Fogler, 1999)

$$X = k_A \cdot \frac{1}{WHSV}$$

Thus, a plot of X versus $1 / WHSV$, for a zero order reaction, will result in a straight line through the origin of gradient k_A .

1.2 First order reaction

In a first order reaction the rate law is as shown in equation A5-6. Equation A5-7 illustrates the relationship between concentration at start of run and conversion.

Equation A5-6: Rate law for a first order reaction (Fogler, 1999)

$$-r_A = k_A \cdot C_A$$

Equation A5-7: Relationship between inlet concentration and conversion (Fogler, 1999)

$$C_A = C_A^o \cdot (1 - X)$$

Equations A5-8 and A5-9 detail the procedure towards deriving a relationship between WHSV and conversion.

Equation A5-8: Expansion of the first order rate law (derived from Fogler, 1999)

$$\frac{W}{F_A^o} = \int_0^X \frac{dX}{k_A \cdot C_A} = \int_0^X \frac{dX}{k_A \cdot C_A^o \cdot (1 - X)} = \frac{1}{k_A \cdot C_A^o} \cdot \ln(1 - X) - \frac{1}{k_A \cdot C_A^o} \cdot \ln(1)$$

Equation A5-9: Relationship between space velocity and conversion for a first order reaction (derived from Fogler, 1999)

$$\ln(1 - X) = k_A \cdot C_A^o \cdot \frac{W}{F_A^o} = k_A \cdot C_A^o \cdot \frac{1}{WHSV}$$

Thus, a plot of $\ln(1 - X)$ versus $1 / WHSV$, for a first order reaction, will result in a straight line through the origin of gradient $(k_A \cdot C_A^o)$.

1.3 Second order reaction

In a second order reaction the rate law is as shown in equation A5-10.

Equation A5-10: Rate law for a second order reaction (Fogler, 1999)

$$-r_A = k_A \cdot C_A^2$$

Equation A5-7 illustrates the relationship between concentration at start of run and conversion, which is substituted into equation A5-10. Equations A5-11 to A5-13 illustrate the procedure towards obtaining a relationship between WHSV and conversion.

Equation A5-11: Expansion of the second order rate law (derived from Fogler, 1999)

$$\frac{W}{F_A^o} = \int_0^X \frac{dX}{k_A \cdot C_A^2} = \int_0^X \frac{dX}{k_A \cdot C_A^{o2} \cdot (1 - X)^2} = \frac{1}{k_A \cdot C_A^{o2}} \cdot \frac{1}{(1 - X)} - \frac{1}{k_A \cdot C_A^{o2}}$$

Equation A5-12: Derivation of the relationship between space velocity and conversion for a second order reaction (derived from Fogler, 1999)

$$\frac{W}{F_A^0} = \frac{1}{WHSV} = \frac{1}{k_A \cdot C_A^0} \cdot \frac{1}{(1-X)} - \frac{1}{k_A \cdot C_A^0} = \frac{1}{k_A \cdot C_A^0} \cdot \left(\frac{1}{1-X} - 1 \right) = \frac{1}{k_A \cdot C_A^0} \cdot \left(\frac{1 - (1-X)}{1-X} \right)$$

Equation A5-13: Derivation of the relationship between space velocity and conversion for a second order reaction, continued from equation A5-11 (derived from Fogler, 1999)

$$\left(\frac{X}{1-X} \right) = k_A \cdot C_A^0 \cdot \frac{1}{WHSV}$$

Thus, plotting $\left(\frac{X}{1-X} \right)$ versus $\left(\frac{1}{WHSV} \right)$ will result in straight line, gradient $\left(k_A \cdot C_A^0 \right)$ for a second order reaction.

2. Calculation of activation energy using low conversion approach (Fogler, 1999)

From the results of the experiments conducted for investigation of variation in temperature effect, the activation energies of the consumption of *m*-cresol and formation of the major primary products were calculated.

Usually a simple method, described by Fogler (1999), is used in activation energy calculations. At low conversions ($\leq 5\%$) the concentrations of the feed compounds can be considered to be unchanged and the specific reaction rate, k_A , can be regarded as being proportional to the conversion, regardless of the order of the reaction. This allows direct determination of the activation energy (E_A), which is related to the preexponential factor or frequency factor (A), the ideal gas constant (R) and absolute temperature (T) in the Arrhenius equation (equation A5-14).

Equation A5-14: Arrhenius equation relating specific reaction rate to frequency factor, activation energy, ideal gas constant and absolute temperature (Fogler, 1999)

$$k_A(T) = A e^{\frac{-E_A}{RT}}$$

Activation energy can be determined experimentally through variation of reaction temperature. Taking the natural logarithm of equation A5-14 gives equation A5-15.

Equation A5-15: Arrhenius equation in logarithmic form relating specific reaction rate to frequency factor, activation energy, ideal gas constant and absolute temperature linearly as a function of the reciprocal temperature (Fogler, 1999)

$$\ln k_A = \ln A - \frac{E_A}{RT}$$

where $R = 0.008314 \text{ kJ / mol} \cdot \text{K}$.

However, the available data, comprised conversion between 19 and 62 %, so this simple approach was no longer applicable.

3. Calculation of activation energy at enhanced conversion for a first order reaction (Levenspiel, 1972)

The method described below was used to calculate activation energy for a first order reaction at enhanced conversion.

The relationship between rate of reaction and conversion for a first order reaction is given in equation A5-6. Combining this with equation A5-7 gives the relationship between rate of reaction and conversion, as shown in equation A5-18, and eventually in equations A5-17 to A5-21, the relationship between activation energy and conversion as a function of the reciprocal temperature.

Equation A5-16: Relationship between rate of reaction and conversion

$$r_A = k \cdot C_A^0 \cdot (1 - X)$$

Equation A5-17: Relationship between rate of reaction and flow rate and conversion

$$r_A = F \cdot X$$

Equation A5-18: Substituting equation A5-18 into equation A5-19

$$F \cdot X = k \cdot C_A^0 \cdot (1 - X)$$

Equation A5-19: Expansion of the specific reaction rate constant

$$k_A = k^0 \cdot e^{\frac{E_A}{RT}}$$

Equation A5-20: Substitution of equation A5-21 into equation A5-20

$$F \cdot X = k^0 \cdot e^{\frac{E_A}{RT}} \cdot C_A^0 \cdot (1 - X)$$

Equation A5-21: Expanded relationship between flow rate, conversion, specific reaction rate, activation energy and temperature

$$\ln F + \ln X = \ln k^0 + \frac{E_A}{T} \cdot \frac{1}{T} + \ln C_A^0 + \ln (1 - X)$$

Equation A5-22: Rearrangement of equation A5-21

$$\ln X - \ln (1 - X) = \ln k^0 + \ln C_A^0 - \ln F - \frac{E_A}{R} \cdot \frac{1}{T}$$

The constant terms in equation A5-22 can be separated, as shown in equation A5-23.

Equation A5-23: Separation of the constant terms in equation A5-22

$$\text{constant} = \ln k^0 + \ln C_A^0 - \ln F$$

The conversion is related to the reciprocal temperature via the activation energy and ideal gas constant, as shown in equation A5-24.

Equation A5-24: Simplified relationship between conversion and reciprocal temperature

$$\ln \frac{X}{(1 - X)} = \text{constant} - \frac{E_A}{R} \cdot \frac{1}{T}$$

Thus, for a reaction of first order, a plot of $\ln \frac{X}{(1 - X)}$ versus $\frac{1}{T}$ will yield a straight line of gradient $-\frac{E_A}{R}$. An example of such a plot is shown in figure A5-1.

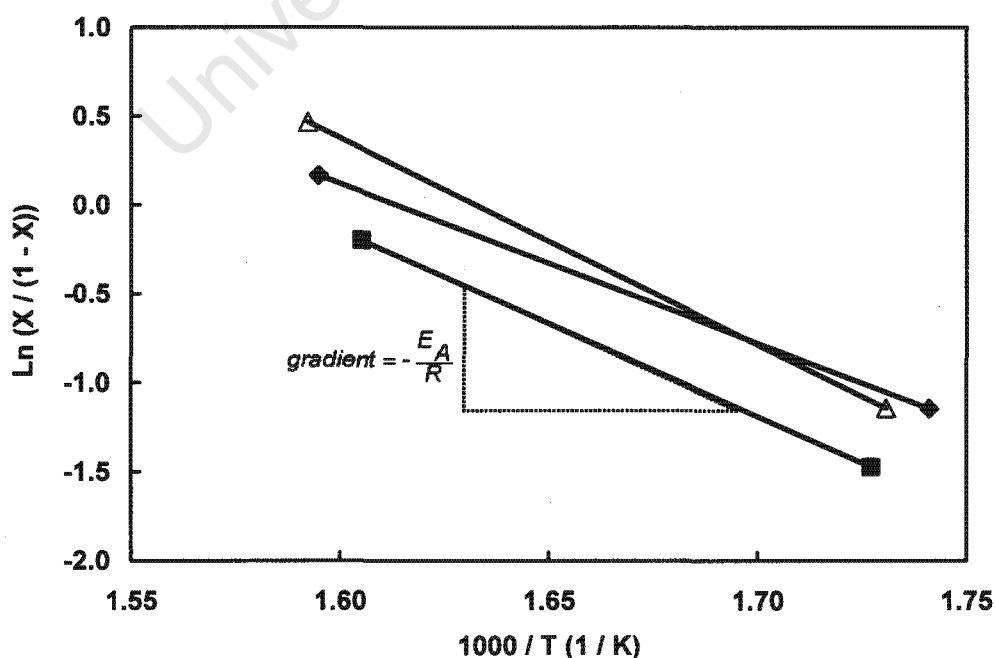


Figure A5-1: Diagram illustrating the method used to calculate the activation energy (E_A) for a first order reaction for conversion of *m*-cresol

Calculations were performed on the results from experiment CM D13. The results from three sets of experiments at 2 different temperatures each (300 and 350°C) were used to calculate the values of activation energy, which then were averaged. The average activation energies that were calculated for a first order reaction are shown in table A5-1.

Table A5-1: Activation energies of different individual reactions from experiment CM D13 of *m*-cresol methylation with methanol over MFI-90, in which reaction temperature was varied from 300°C to 350°C. These data have been calculated assuming 1st order reaction, as per the method in Levenspiel, 1972.

Reaction	Activation Energy (E_A) (kJ / mol)
<i>m</i> -Cresol + methanol, overall conversion	86
<i>m</i> -Cresol + methanol → 2,5-xylanol + water	72
<i>m</i> -Cresol + methanol → 3,4-xylanol + water	54
<i>m</i> -Cresol + methanol → 2,3-xylanol + water	25
<i>m</i> -Cresol + methanol → sum of major xylanol isomers + water	59

In calculating the activation energy of formation of individual primary products, an equation analogous to equation 5-24 was used, where conversion X was replaced by the respective yield Y .

4. Calculation of activation energy at enhanced conversion for a second order reaction (Levenspiel, 1972)

The method described below was used to calculate activation energy for a second order reaction at enhanced conversion.

The relationship between rate of reaction and conversion for a second order reaction is given in equation A5-10. Combining this with equation A5-7 will give the relationship between rate of reaction and conversion, as shown in equation A5-25.

Equation A5-25: Relationship between conversion and temperature

$$r_A = k \cdot (C_A^0)^2 \cdot (1 - X)^2$$

Using equation A5-17, it is possible to obtain a relationship between flow, conversion, specific reaction rate and concentration (equation A5-26).

Equation A5-26: Relationship between conversion and temperature

$$F \cdot X = k \cdot (C_A^0)^2 \cdot (1 - X)^2$$

Substituting equation A5-19 into equation A5-6, produces the relationship given in equation A5-27 and eventually equations A5-28 and A5-29.

Equation A5-27: Relationship between conversion, activation energy and temperature

$$F \cdot X = k^o \cdot e^{\frac{E_A}{RT}} \cdot (C_A^o)^2 \cdot (1-X)^2$$

Equation A5-28: Expanded logarithmic relationship between flow rate, conversion, specific reaction rate, activation energy and temperature

$$\ln F + \ln X = \ln k^o + \frac{E_A}{T} \cdot \frac{1}{T} + 2 \cdot \ln C_A^o + \ln (1-X)^2$$

Equation A5-29: Rearrangement of equation A5-28

$$\ln X - \ln (1-X)^2 = \ln k^o + 2 \cdot \ln C_A^o - \ln F - \frac{E_A}{R} \cdot \frac{1}{T}$$

The constant terms in equation A5-29 can be separated, as shown in equation A5-30.

Equation A5-30: Separation of the constant terms in equation A5-30

$$constant = \ln k^o + 2 \cdot \ln C_A^o - \ln F$$

The conversion is related to reciprocal temperature via the activation energy and ideal gas constant, as shown in equation A5-31.

Equation A5-31: Relationship between conversion, activation energy and temperature

$$\ln \frac{X}{(1-X)^2} = constant - \frac{E_A}{R} \cdot \frac{1}{T}$$

Thus, for a reaction of second order, a plot of $\ln \frac{X}{(1-X)^2}$ versus $\frac{1}{T}$ will yield a straight line of gradient $-\frac{E_A}{R}$. An example of such plot is shown in figure A5-2.

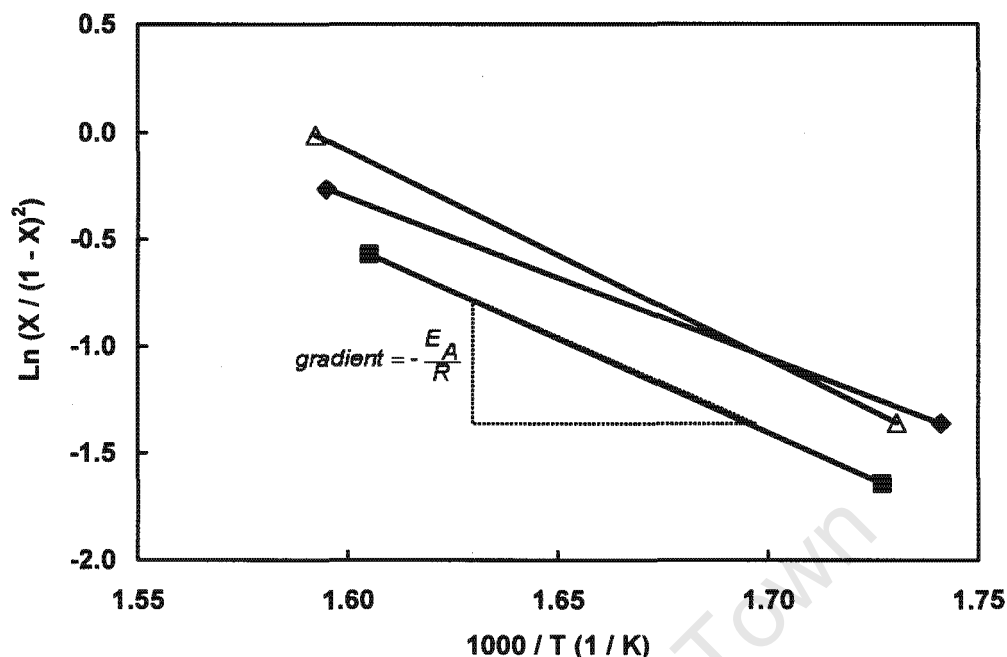


Figure A5-2: Diagram illustrating the method used to calculate the activation energy (E_A) for a second order reaction for conversion of *m*-cresol

Calculations were performed on the results from experiment CM D13, again from 3 pairs of data and then averaged. In calculating the activation energy of formation of individual primary products, an equation analogous to equation 5-31 was used, where conversion X was replaced by the respective yield Y .

The activation energies that were calculated for a second order reaction are shown in table A5-2.

Table A5-2: Activation energies of different individual reactions from experiment CM D13 of *m*-cresol methylation with methanol over MFI-90, in which reaction temperature was varied from 300°C to 350°C. These data have been calculated assuming 2nd order reaction, as per the method in Levenspiel, 1972.

Reaction	Activation Energy (E_A) (kJ / mol)
<i>m</i> -Cresol + methanol, overall conversion	72
<i>m</i> -Cresol + methanol → 2,5-xyleneol + water	68
<i>m</i> -Cresol + methanol → 3,4-xyleneol + water	51
<i>m</i> -Cresol + methanol → 2,3-xyleneol + water	24
<i>m</i> -Cresol + methanol → sum of major xyleneol isomers + water	53

Appendix 6: Normalisation of Conversion

In experiments to compare the effect of *m*-cresol : methanol feed ratio the feed composition was varied, while the pump rate was controlled at similar rate for different feed compositions since it was already working at the lower end of possible settings and the digital setting did not allow finer tuning. Anyway, this ensured that the total liquid feed rate to the apparatus (ml / min) remained constant for different methanol : *m*-cresol feed ratios, but the weight hourly space velocity of the *m*-cresol did not remain constant.

When comparing the effect of a primary parameter, such as methanol : *m*-cresol feed ratio, all other secondary parameters, including weight hourly space velocity should be kept constant so as not to influence the effect of the primary parameter.

In this set of experiments the weight hourly space velocity (WHSV) did not remain constant. For this reason the WHSV was normalised to the median WHSV (or WHSV for methanol : *m*-cresol feed ratio of 1 : 1) with the new “normalised” WHSV being defined $WHSV_{norm}$ for each set of methanol : *m*-cresol feed ratio experiments. This required linear adjustment of WHSVs for methanol : *m*-cresol feed ratios of 2 : 1 and 1 : 2, respectively, to $WHSV_{norm}$.

Conversion and selectivity were assumed to vary linearly between nearby data points see figure A6-1). Thus the normalisation was conducted using data from the closest data points to that which was normalised.

Following is an illustration detailing how these calculations were performed (refer to equations A6-1 and A6-2). Table A6-1 contains experimental data for an experiment in which methanol : *m*-cresol feed ratio was varied for two constant pump rates (0.02 and 0.04 ml / min).

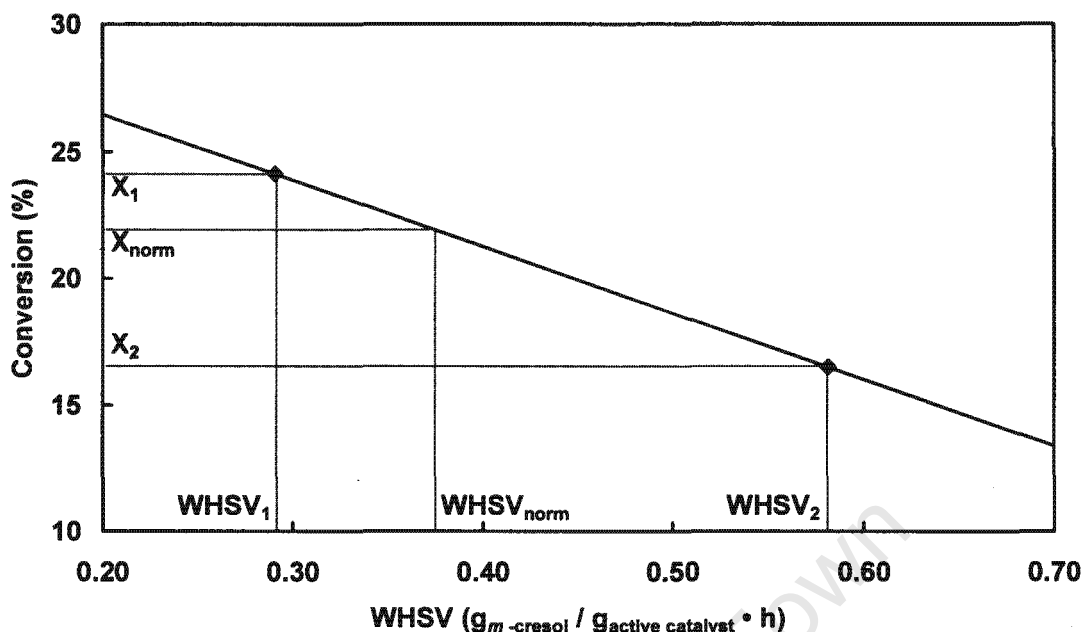


Figure A6-1: Diagram illustrating the use of linear interpolation to determine “normalised” conversion X_{norm} for “normalised” $\text{WHSV}_{\text{norm}}$. Refer to equation A5-1 for the calculation involved

Equation A6-1: Method used to calculate the “normalised” conversion, X_{norm} , using nearby data points. Please refer to figure A5-1.

$$X_{\text{norm}} = X_1 + \frac{(X_2 - X_1)}{(\text{WHSV}_2 - \text{WHSV}_1)} * (\text{WHSV}_{\text{norm}} - \text{WHSV}_1)$$

In the following example, the conversions obtained at WHSV s of 0.29 and 0.43 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$ are being used to calculate normalised conversion X_{norm} at $\text{WHSV}_{\text{norm}}$ of 0.37 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$ (refer to equation A6-2).

Equation A6-2: An example showing the calculation to determine normalised conversion X_{norm} for *m*-cresol methylation at normalised $\text{WHSV}_{\text{norm}}$ of 0.37 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$

$$X_{\text{norm}} = 24.13 + \frac{(16.51 - 24.13)}{(0.58 - 0.29)} * (0.37 - 0.29) = 22.02 \%$$

For normalisation of the selectivity to 2,5-xylenol at $\text{WHSV}_{\text{norm}}$ of 0.37 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$, a similar method was used, refer to equation A6-3.

Equation A6-3: An example showing the calculation to determine normalised selectivity to 2,5-xylenol for *m*-cresol methylation at normalised $\text{WHSV}_{\text{norm}}$ of 0.37 $\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$

$$\text{Selectivity to 2,5 - xylenol}_{\text{norm}} = 12.73 + \frac{(12.75 - 12.73)}{(0.58 - 0.29)} * (0.37 - 0.29) = 12.73 \text{ mol}\%$$

Table A6-1: Original and normalised WHSV, conversion and selectivity to 2,5-xyleneol from variable methanol : *m*-cresol feed ratio experiments for methylation of *m*-cresol with methanol over MFI-90 at 300°C. Data extracted from experiment CM D12.

$\text{WHSV}_{\text{original}}$ ($\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$)	$\text{WHSV}_{\text{norm}}$ ($\text{g}_{m\text{-cresol}} / \text{g}_{\text{active catalyst}} \cdot \text{h}$)	Methanol : <i>m</i> - cresol molar feed ratio	$\text{Conversion}_{\text{original}}$ (%)	$\text{Conversion}_{\text{norm}}$ (%)	$\text{Selectivity}_{\text{original}}$ to 2,5-xyleneol (mol %)	$\text{Selectivity}_{\text{norm}}$ to 2,5-xyleneol (mol %)
0.29	0.37	2 : 1	24.13	22.01	12.73	12.73
0.37	0.37	1 : 1	24.18	24.18	14.21	14.21
0.43	0.37	1 : 2	18.67	21.46	13.65	14.00
0.43	0.37	1 : 2	18.88	21.61	13.61	13.97
0.58	0.74	2 : 1	16.51	14.57	12.75	12.54
0.74	0.74	1 : 1	15.41	15.41	13.10	13.10
0.86	0.74	1 : 2	12.09	13.98	12.50	12.81