Transalkylation of Higher Methylphenols with Phenol to produce Cresols and Xylenols

by

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SYNOPSIS

South Africa has large coal gasification capacities and thus the country is one of the largest producers of 'natural' phenolics. However, the phenolics stream derived from their coal gasification plants does not only contain much sought after phenol, cresols and xylenols but is also rich in a multitude of higher polymethylated phenol isomers, which are of comparatively low economic value. At present it is only the phenolic compounds, which are contained in the aqueous by-product stream from the gasifier, which are extracted and worked up. Nonetheless, it has recently been announced that in the near future the raw naphtha by-product stream from the gasifier, which also contains phenolics, will be processed to extract these compounds. This will further increase the availability of higher phenolics. However, the low value mixtures of C_{9+}-polymethylphenols obtained from this work-up still carry the potential for subsequent value enhancement.

The idea behind this research was to add value to such C_{9+}-polymethylphenol isomer mixtures by converting them into high value cresols and xylenols via transalkylation with phenol over acid zeolite catalysts. This would comprise recovery of the valuable aromatic (phenolic) OH-groups present in the constituents of the C_{9+}-phenolics fraction and also make use of the C_{9+}-polymethylphenols as an active – and cheap – reagent for the methylation of the phenol, due to the activation of their aromatic rings by the OH-group.

Transalkylation reactions were carried out in liquid phase at 60 bar in a continuously operated, isothermal, tubular laboratory scale reactor over 6 g of acid zeolite catalyst in crystal powder or extruded form. Three commercially available acid zeolite catalysts were screened, H-MFI, H-MOR and H-BEA. Of the three, the latter with a molar SiO_2 / Al_2O_3 ratio of 25 was chosen for most of the subsequent optimisation studies due to its generally better performance.

Investigations into the effects of reaction conditions were carried out by using a phenol : 2,5-xylenol feed mixture. Reaction temperature, weight hourly space velocity and feed ratio were varied from 250 to 450°C, 0.113 to 0.45 h^{-1} and 1 : 1 to 20 : 1, respectively. Additional investigations at 350°C, varying space velocity in the same range and with a molar feed ratio of 1 : 1 were performed using a phenol : 2,3,6-trimethylphenol feed mixture. In order to simulate a technical C_{9+}-phenolics feed stream, a mixture of polymethylated phenols was produced via alkylation of lower methylphenols with methanol over an acid catalyst. This simulated technical mixture was applied with excess phenol in a 20 : 1 molar ratio feed mixture and transalkylated at 350°C, varying space velocity as above.

Isomerisation of individual higher methylated feed compounds (2,5-xylenol and 2,3,6-trimethylphenol) via a 1,2-methyl shift reaction was found to be rather rapid compared to the actual transalkylation step and thus, to some extend, preceding transalkylation.

Significant yields and selectivities of the most desired cresols were obtained when converting the binary mixtures as well as a feed comprising phenol and the simulated technical mixture. For instance, transalkylation of a 1 : 1 molar ratio mixture of 2,3,6-trimethylphenol with phenol at 350°C and a weight hourly space velocity of 0.113 h^{-1}, at about 40 % phenol conversion (i.e. with the reaction mixture not yet close to the thermodynamic equilibrium carbon number distribution) effects cresol and xylenol yields of about 15 mol% each. From the 20 : 1 molar ratio feed of phenol and the simulated technical mixture, at the same conditions and with not yet equilibrated carbon number distribution, about 10 mol% cresols were obtained.

It appeared that the isomer distribution in the cresol fraction is kinetically controlled with the transfer of the methyl group onto the phenol molecule following basic chemical rules, namely, preferred alkylation in the o- and p-positions. This results in a comparably high percentage of rather low market

value o-cresol and a low percentage of high market value m-cresol. Significantly less m-cresol is forming than in thermodynamic equilibrium and apparently most of it is only forming as a secondary product via isomerisation of o- and p-cresol. Even so, experimental results as well as theoretical calculations suggest that a large phenol excess is not required to achieve a product carbon number distribution dominated by cresols as well as satisfactory cresol yields and selectivities.

Significant selectivities to cresols and xylenols were also obtained when converting the phenol-with-2,3,6-trimethylphenol and the phenol-with-simulated technical feed mixtures, always forming a mixture of cresol and xylenol isomers. However, a conclusive interpretation of the obtained xylene isomer distributions and a conclusion on the reaction pathways was not possible. Nonetheless, experimental results as well as thermodynamic equilibrium calculations confirm that the ratio of cresols to xylenols is eventually determined by the excess of phenol applied.

Some less favourable aspects of the suggested process were identified, for example (i) the carbon number distribution and thus cresol selectivity is limited by thermodynamic equilibrium, corresponding to the given excess of phenol, and will limit the maximum once through yield of cresol, (ii) between half and two thirds, depending on conditions, of the converted phenol in the 20 : 1 molar phenol : simulated technical mixture feed reacted to diphenylether (this would represent a significant loss of valuable OH-groups and aromatic rings if it was not recycled or its formation suppressed by e.g. applying a lower phenol excess or co-feeding water), (iii) significant percentages of heavy compounds build-up when operating at too high a reaction temperature (above about 375°C) and (iv) recycling of unconverted feed and certain products or product fractions (in the first instance diphenylethers) appears to be unavoidable.

With respect to a final judgement of the suggested process it should be noted that the alternative 'direct' routes to cresols, namely, the alkylation of phenol with methanol, are not 'clean' at all, also requiring rather severe conditions. In particular when high selectivity towards m-cresol is the goal, a mixture of compounds is produced which requires costly separation, and of which much is undesired and of low value.

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SYMBOLS AND GLOSSARY

Only very few symbols and acronyms are used in this thesis and they are explained immediately.

Chapter 1

INTRODUCTION

As a result of political issues the country faced in the 70's and early 80's, South Africa has large coal gasification capacities and thus the country is one of the largest producers of natural phenolics. However, the phenolics stream derived from their coal gasification plants does not only contain much sought after phenol, cresols and xylenols but it is also rich in higher phenols (see table 1-1) which are of low economic value as compared to phenol, cresols and xylenols.

Table 1-1: Yield and distribution of phenolic compounds in coal gasifier tar from water-free bituminous coal (800 – 900°C, 20 bar) [Fiege, 2003]

Constituent	*Yield (kg/ton of coal)*	*Distribution (wt % phenolics)*
Phenol	0.14	4
Cresols	0.63	20
Xylenols	0.78	24
Higher phenols	1.67	52

From lignite, as gasified by Dakota Gasification company in the united states, higher yields of ca. 6.1, 5 and 3 kg/ton of coal of phenol, cresols and xylenols, respectively, are reported [Fiege, 2003].

Phenol, cresols and xylenols have a wide range of applications as starting materials for various products. These include use for making herbicides, insecticides, disinfectants, preservatives, antioxidants, perfumes and fragrances, and various pharmaceuticals, for example, chemotherapeutics like trimethoprim which can be used for treatment of "travelers" diarrhea. The most important field

of application for phenol, the individual cresol isomers, technical mixtures of cresols isomers and certain xylenols (on the first hand 2,6-xylenol) is the production of various modifications of phenolic resins by condensation with formaldehyde, for example, for making engineering plastics [Fiege, 2003]. Higher polyalkylated, in particular polymethylated phenols such as the constituents of "creosote" have limited applications and these mixtures are usually used in formulations of impregnating oil, used for wood protection [Fiege, 2003]. Hence the reason why cresols and xylenols have a higher market value than the higher phenols. Consequently, routes to conversion of low value, higher phenolic compounds into the high value cresol/xylenol pool are of potential commercial interest.

1.1 Cresols and xylenols from coal tars and refinery caustics

Traditionally cresols and xylenols were obtained from high temperature coke oven tar. In the UK cresols are also produced from low temperature coal tars obtained in the production of smokeless solid fuels from coal (Coalite process). By the 1990s all of these tars had become far less abundantly available. In recent years the largest single source of "natural" cresols and xylenols has been Sasol (35 000 – 55 000 t/a). Their cresols and xylenols are produced in the pressure gasification of bituminous coal by Lurgi gasifiers to produce syngas for their Fischer-Tropsch synthesis facilities [Fiege, 2003]. Another important source of phenolics from coal gasification is Dakota Gasification Inc. in the United States, who are gasifying lignite in Lurgi gasifiers. Cresols and xylenols are also recovered from spent refinery caustics from naphtha sweetening process. However, this has so far been confined to the United States. In other places, the potential yield of cresols from spent refinery caustics is insufficient for economical processing or no such caustics are produced at all [Fiege, 2003].

1.2 Synthetic production of cresols

Cresols and xylenols have been increasingly produced synthetically since 1965 when the recovery from coal tar and spent refinery caustics had become insufficient to meet the increasing demand. The synthetic processes that are now in use for commercial cresol manufacturing are (i) alkali fusion of toluenesulphonates, (ii) alkaline chlorotoluene hydrolysis, (iii) splitting of cymene hydroperoxide and (iv) methylation of phenol. These processes produce different isomer distributions and hence are all of individual importance [Fiege, 2003].

1.2.1 Alkali fusion of toluenesulphonates

Toluene is sulphonated with concentrated sulphuric acid and the resulting sulphonates are hydrolysed to cresol. This process is mainly used to produce p-cresol. Normally a mixture of the following composition is obtained: 6 -12 % o-cresol, 6 -12 % m-cresol and 80 - 85 % p-cresol. The high p-selectivity results from the toluene sulphonation reaction being sterically hindered in the o-position and the m-position being less reactive. The principal disadvantage of this method is the unavoidable production of sodium sulphite as a co-product in aqueous solution [Fiege, 2003].

1.2.2 Alkaline chlorotoluene hydrolysis

This process produces cresols with high m-cresol content. With a 1:1 o/p-chlorotoluene mixture (which is obtained when a 1:1 molar mixture of toluene and chlorine are reacted over an iron (III) chloride catalyst), the o-, m- and p-cresol isomers are produced in the ratio 1:2:1, i.e. close to thermodynamic equilibrium distribution [Fiege, 2003].

1.2.3 Cymene hydroperoxide cleavage

The process is analogous to the cumol (Hock) process for phenol manufacture, just using cymene isomers (isopropyl-toluenes) oxidising them and hydrolysing the resulting peroxides to cresols. This process allows the production of m- or p-cresol or a mixture of both from the corresponding individual cymene isomers or mixtures thereof. It is not suitable for the production of o-cresol. This is because the corresponding cymene isomer (o-cymene) can hardly be oxidized to cymene hydroperoxide. The o-isomer also inhibits the oxidation of the other cymene isomers [Fiege, 2003].

1.2.4 Methylation of phenol

This process can be carried out at various temperatures in either the liquid phase or the vapour phase and over a variety of different types of catalysts. Processes, over basic catalysts such as MgO or FeV/SiO_2, also amphoteric Al_2O_3 at low temperature, produce pure o-cresol / 2,6-xylenol mixtures. 2,6-Xylenol is almost entirely produced by this process. The main product over acid catalysts such as SiO_2/Al_2O_3, acid zeolites or Al_2O_3 at high temperature, is m-cresol with some o- and p-cresol, also 2,6-, 2,4- and 2,5-xylenol [Fiege, 2003] .

1.2.5 Other synthetic processes

The increase in demand for cresols led to the development of several other synthetic processes. However these processes are not or not yet being used industrially. Examples of such processes are the Gulf Oxychlorination, Oxidative Decarboxylation of Methylbenzoic Acids, Hydroxylation of the aromatic ring (direct hydroxylation of toluene) and Oxidative Methylation of Toluene to cresols [Fiege, 2003].

1.3 Synthetic production of xylenols

Synthetic processes that are now in use for xylenols manufacture are (i) Phenol methylation, (ii) Demethanisation of Isophorone, (iii) Dimethylcumene Hydroperoxide Cleavage, (iv) Alkaline Chloroxylene Hydrolysis and (v) Alkali Fusion of Xylenesulphonates.

1.3.1 Phenol methylation

See section 1.2.4.

1.3.2 Demethanisation of isophorone

3,5-Xylenol is normally not a product of methylation processes and it is only isolated in limited amounts from natural xylenol mixtures. This xylenol isomer is produced by demethanisation of isophorone, which is the product of cyclic aldol condensation of acetone. The reaction is carried out in the vapour phase in a multitubular reactor at 600 ^{o}C and 0.1 kPa and space velocities around 0.5 h^{-1} (LHSV). Toluene, xylene, mesitylene, dihydroisophorone, m-cresol, 2,4- and 2,5-xylenol and 2,3,5-trimethylphenol are formed as by-products [Fiege, 2003].

1.3.3 Dimethylcumene hydroperoxide cleavage

3,5-xylenol is produced from this process by oxidation of 3,5-dimethylcumene to 3,5-dimethylcumene hydroperoxide which is then cleaved. This method is more expensive than the analogous cymene-cresol process (section 1.2.3) because of the additional methyl group, which leads to more side reactions [Fiege, 2003].

1.3.4 Alkaline chloroxylene hydrolysis

In this process, chloroxylenes are hydrolysed to xylenols. Mixtures of 2,4- and 3,5-xylenol are obtained from 2,4- or 3,5-dimethylchlorobenzene. These can then

be separated by distillation. 2,3- and 3,4-xylenols can be obtained from the alkaline hydrolysis of 2,3- and 3,4-dimethylchlorobenzene [Fiege, 2003].

1.3.5 Alkali fusion of xylenesulphonates

In this process 2,4-xylenol is produced from the sulphonation of m-xylene with sulphuric acid or chlorosulphuric acid followed by hydrolysis. From this, 3,5-xylenol can also be obtained by changing operating conditions and using excess alkali. Sulphonation of p-xylene leads to production of 2,5-xylenol. 3,4-xylenol is obtained from sulphonation of o-xylene. Under mild sulphonation conditions, it is possible to produce 2,3-xylenol from o-xylene as well [Fiege, 2003].

1.3.6 Other synthetic processes

Other synthetic processes for the production of xylenols have also been developed but are not or not yet used industrially. These processes include the Gulf Oxychlorination process from which 2,6- and 2,4-xylenols can be obtained [Fiege, 2003].

1.4 Lurgi coal gasification process

South Africa's source of phenolics is Sasol's Lurgi coal gasification process. In this process, coal is contacted in the gasification reactor with a gasification agent (a mixture of superheated steam and pure oxygen) in countercurrent mode. In this way, coal pyrolysis products are driven from the coal by the hot, raw syngas and obtained together with the syngas over the top [Schilling et al., 1981]. The major product streams obtained in this process are shown in figure 1-1.

It is from the aqueous condensate stream, the "gasification liquor" (figure 1-1) that phenolics are currently obtained. The recovery of phenolics from this stream is done by the Phenosolvan process (see section 1.4.1). Sasol has announced

that it is planning to also extract the phenolics fraction from the raw naphtha stream in the near future [du Preez, 2003].

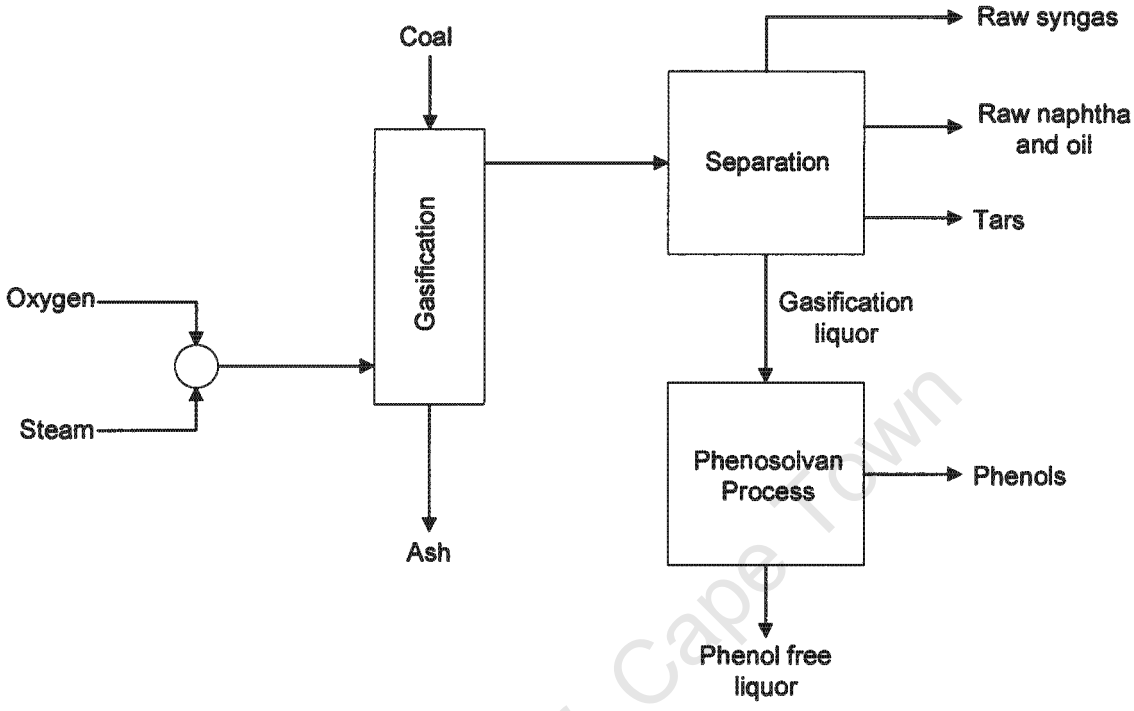


Figure 1-1: Schematic diagram of the Lurgi coal gasification and phenolics recovery process [adapted from Schilling et al., 1981]

1.4.1 Phenosolvan process

In the Phenosolvan process, the aqueous stream from the gasification process is passed through a multistage countercurrent extractor. In the extractor, phenols are extracted with an immiscible polar organic solvent, usually butylacetate or diisopropylether. The extract, containing phenols and the solvent, is then distilled to remove the solvent. Remaining solvent, contained in the raw phenol fraction after distillation, is recovered by steam stripping [Duncan, 1998].

A typical raw Phenosolvan extract in addition to the phenolic compounds contains approximately 20% to 30% pitch, neutral oils (1% to 4%), tar bases (1% to 3%) and water (2% to 6%). This raw phenolics mixture is further purified

[Duncan, 1998]. Table 1-2 gives the relative weight percentage distribution of the phenols in a depitched Phenosolvan extract.

Table 1-2: Typical composition of a depitched Phenosolvan extract from the liquors from steam gasification of coal [Stönner, 1989]

Compound	*Weight Percentage*
Phenol	45
Cresols	30
Xylenols	6
Polyhydric and other phenols	10
Pyridine bases	1
Neutral oil, pitch	5
Water	3

1.4.2 A new process of phenolics recovery from coal pyrolysis naphthas

In addition to the quantities dissolved in the gasification liquor (the aqueous phase) a part of the total phenolic compounds produced by the coal gasifier is contained in the liquid organic by-products fractions, e.g., the raw naphtha. Venter and Nieuwoudt [2002] have developed a process for the recovery of phenolics from such coal pyrolysis naphthas. This process comprises a solvent-solvent extraction with a solvent system consisting of a phenolics selective solvent mixture and hexane as a countersolvent. It was discovered that phenolics selective solvents are those that contain hydroxyl groups positioned on the molecules' backbones in such a way as to facilitate hydrogen bonding with more than one phenolic molecule at a time. The best commercially available solvent identified was triethylene glycol mixed with water.

However, it is not known yet whether Sasol's naphtha extraction process will be identical with or similar to the Venter / Nieuwoudt process or not.

Chapter 2

LITERATURE REVIEW

2.1 Phenol

Phenol (figure 2-1) occurs as a free component or as an addition product in many natural products. For example, it is a component of lignin.

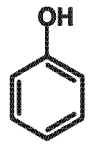


Figure 2-1: Chemical structure of phenol

In industrial production, phenol was initially extracted exclusively from hard coal tar. Following the rise in the phenol consumption, synthetic production routes were introduced during the 1960's. A number of processes for the synthetic production of phenol have been developed. Of all these processes, the most important, industrially, are (i) alkylation of benzene with propene to isopropylbenzene (cumene), oxidation of the cumene to the corresponding tert.-hydroperoxide, and hydrogenolytic cleavage to phenol and acetone (Hock process) and (ii) toluene oxidation to benzoic acid and subsequent oxidising decarboxylation to phenol (Dow process). Other processes were abandoned for environmental or economic reasons or have never been implemented industrially [Fiege, 2003].

Phenol has achieved considerable importance as a starting material for numerous intermediates and finished products. Most of it is processed further to give phenol-formaldehyde resins [Fiege, 2003]. Its major physical properties are given in appendix A.

2.2 Cresols

Cresols, or methylphenols, occur in three isomeric forms (figure 2-2).

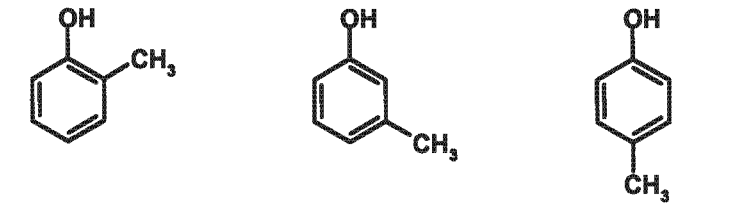


Figure 2-2: Chemical structures of the cresol isomers

Cresols are widely distributed in nature. They are formed as metabolites of various organisms including the human body, e.g., contained in urine. Cresols are also found in extracts and vapour distillates of many plants, e.g., jasmine flower oil. Small amounts of cresols are found in certain foods and drinks, e.g., in tomatoes [Fiege, 2003].

Cresols are important chemical raw materials. Originally they were obtained only from coal tar. After World War II they were also obtained from spent refinery caustics. Cresols have been produced synthetically on an increasing scale since the 1960s. Today the largest amount of "natural" cresols, i.e., those derived directly from processing natural feed stocks such as coal, is obtained by Sasol in South Africa (35 000 – 55 000 t/a) from liquid by-product streams of the pressure gasification of bituminous coal by the Lurgi process [Fiege, 2003]. The major physical properties of the cresols are given in appendix A.

2.3 Xylenols

Xylenols, or dimethylphenols, occur in six isomeric forms, as shown in figure 2-3.

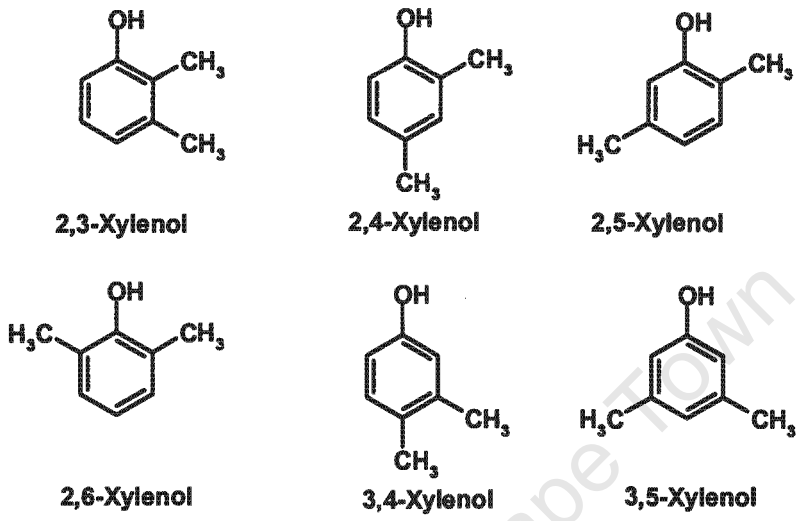


Figure 2-3: Chemical structures of the xylenol isomers

Xylenols are present in natural products such as essential oils of conifers, tea, tobacco smoke and in various smoked foods [Fiege, 2003].

Xylenol mixtures are obtained mainly in the United States, South Africa and Europe from spent refinery caustics and coal tars. The most important isomer, economically, is 2,6-xylenol of which, however, only relatively small amounts are obtained from coal tars. 2,6-Xylenol is therefore almost entirely produced synthetically by phenol methylation [Fiege, 2003]. The major physical properties of the xylenols are given in appendix A.

2.4 Trimethylphenols

Trimethylphenols occur in six isomeric forms, as shown in figure 2-4.

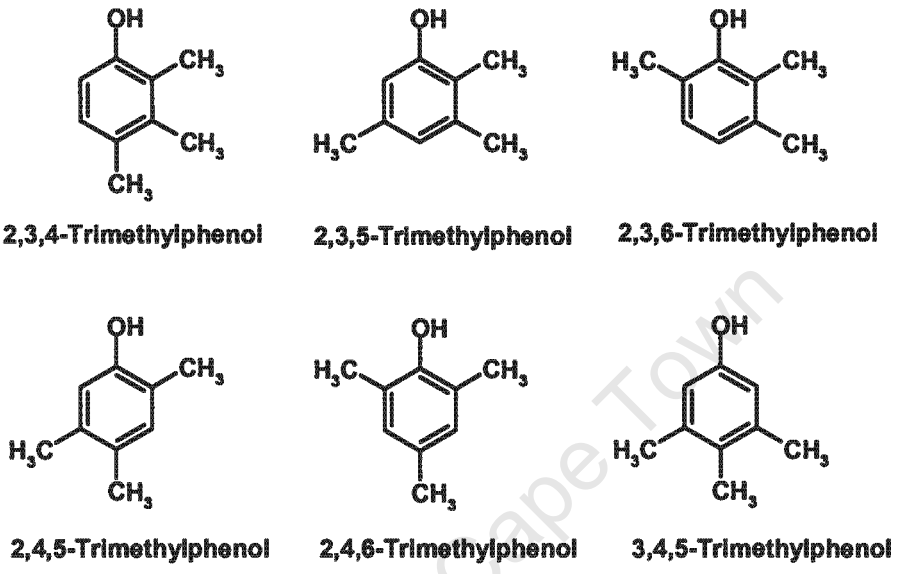


Figure 2-4: Chemical structures of the trimethylphenol isomers

Trimethylphenols are found in natural products such as wood creosote derived from beechwood and the resin from leaves of the creosote bush (Larrea). Trimethylphenols are also found in coal tar derived creosote. Trimethylphenols are not separated from these creosotes. The creosote is usually marketed for wood protection [Gerberding, 2002].

Individual trimethylphenol isomers are produced synthetically. 2,3,6-Trimethylphenol and 2,4,6-trimethylphenol are produced in small amounts as by-products during the synthesis of cresols and xylenols by methylation of phenol. 2,3,6-trimethylphenol can also be produced synthetically by selective methylation of m-cresol with methanol. 2,3,5-Trimethylphenol can be obtained by methylation of 3,5-xylenol in the presence of ortho-selective catalysts [Fiege, 2003]. The major physical properties of the trimethylphenols are given in appendix A

2.5 Chemistry of phenols

2.5.1 Reactivity of phenols

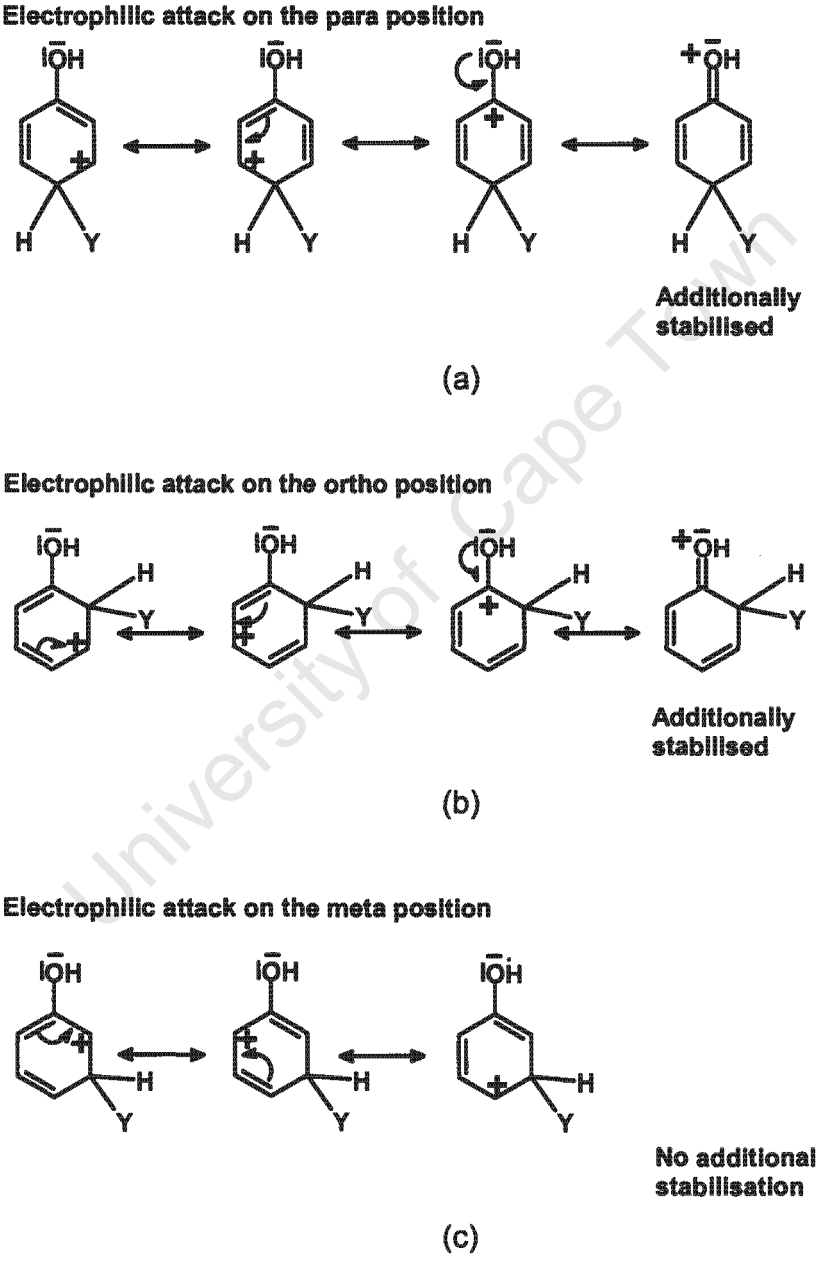
Alkylation of phenol proceeds via an electrophilic attack by the alkylating agent. This attack can either be on the ring (C-alkylation to cresol (assumes alkylating agent is methanol)) or on the hydroxyl group (O-alkylation to anisole, the methyl-phenyl ether (assumes alkylating agent is methanol)). On less acidic catalysts O-alkylation dominates [Parton et al., 1989]. In reaction between phenol and methanol over an alumina catalyst at 200 °C, the attack on the hydroxyl group was found to be 2 times faster than the attack on the ring [Santacesaria et al., 1990a]. This ratio was found to decrease with increasing temperature because the carbon in the ring is alkylated over alumina with a higher activation energy of 134 kJ / mol compared to 67 kJ / mol for oxygen alkylation. On the other hand, for the alkylation of phenol with methanol at 300 °C, Pierantozzi and Nordquist [1986] calculated that at thermodynamic equilibrium, cresol formation is favoured over anisole by a factor 10^4.

A hydroxyl group on a benzene ring is activating the ring for electrophilic attack, e.g., by a carbenium ion, compared to benzene [Morrison and Boyd, 1987, and Sykes, 1986a]. The hydroxyl group 'pumps' negative charge into the ring, by mesomeric effect, stabilising the carbenium ion intermediate that forms, in addition to just the spreading of the positive charge over the ring as in benzene (figures 2-5 (a) to (c)). Additional alkyl groups on the ring, by electron donating inductive effects, reinforce activation, though their contribution is weak compared to that of the hydroxyl group.

2.5.2 Selectivity of ortho-, oara- and meta-substitution of the phenol ring under kinetic control

An electrophilic attack on the phenol ring shows a kinetic preference for the ortho and para positions [Morrison and Boyd, 1987, and Sykes, 1986a]. This is

because of the o/p-directing behaviour of the hydroxyl group. Mesomeric / resonance / limiting structures of the carbenium ions that result from the electrophilic attack on the phenol ring and whose relative stabilities determine the orientation of attack, are shown in figures 2-5 (a), (b) and (c).



Figures 2-5 (a), (b) and (c): Transition state resonance structures from electrophilic attack on the phenol ring [Morrison and Boyd, 1987, and Sykes, 1986a]

As shown in figures 2-5 (a) and (b), an electrophilic attack at the ortho and the para positions of the phenol ring results in a cationic intermediate whose positive charge can be stabilised by the lone electron pairs of the oxygen atom in the hydroxyl group. An attack at the meta positions results in an intermediate with a charge at a position which cannot be stabilised by the lone electron pairs of the oxygen atom, see figure 2-5 (c). Thus o- and p- attack is kinetically favoured.

The alkyl groups in alkylated phenols, due to their inductive effects, induce some weak ortho and para selective preferences (relative to their own position) which adds favourably or not to the effect of the hydroxyl group.

A statistical ratio of 2:1 of ortho : para substitution of the phenol ring is expected. This is because of the fact that there are two ortho positions to one para position per phenol ring. However, this does not necessarily hold. Based on resonance considerations, the attack on the para position should be slightly favoured [O'Connor et al., 1996]. This would result in an o- : p- ratio of > 2:1.

As the attacking electrophile increases in size there will be increasing interaction (steric hindrance) between the electrophile and the hydroxyl group on the phenol molecule in the transition state for attack at the ortho position. This lowers the relative proportion of the o-product and would therefore result in an o- : p- ratio < 2:1 [Sykes, 1986a].

Another reason why the 2:1 ratio does not hold is the fact that primary alkylation of phenol proceeds via both O-alkylation and C-alkylation routes with subsequent internal rearrangement of the O-alkylation products to ortho substituted phenol products in secondary reactions. This would result in an o- : p- ratio > 2:1 [Sykes, 1986a, and Xu et al., 1997].

With increasing conversion, the distribution of the o-, p- m-substituted products does no longer only depend on the relative rates at which they are initially formed

(kinetics), since due to secondary reactions (e.g. isomerisation), the thermodynamic stability of the products forming plays an increasing role in determining the proportions [Sykes, 1986a]. This would eventually result in an o- : p- ratio slightly higher than 2:1 and an increasing percentage of m-cresol, see section 2.7.1.

2.5.3 Transformation of cresols and xylenols

Cresols and xylenols are transformed through two main routes, a unimolecular isomerisation via a 1,2-methyl shift mechanism and a bimolecular disproportionation or transalkylation [Parton et al., 1989]. The mechanism of the acid catalysed 1,2-methyl shift goes probably through a transition state involving a protonated cyclopropane ring (figure 2-6) analogous to the carbocation transition state for paraffins skeleton isomerisation [Sykes, 1986b].

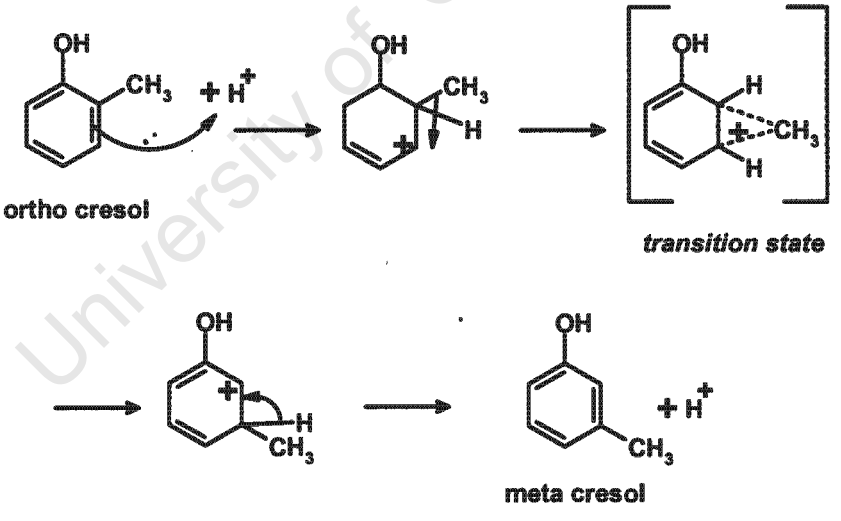


Figure 2-6: 1,2-methyl shift mechanism for cresols and xylenols isomerisation [adapted from Sykes, 1986b, and Böhringer, 2006]

2.5.4 Phenolics transalkylation

Transalkylation of higher methylphenols with phenol has been reported to occur in the presence of acid alkylating catalysts to give a product consisting mainly of o-cresol, together with small amounts of m- and p-cresol. This reaction is reported to proceed either in the liquid or in the vapour phase and in a temperature range of 400 – 500 °C. The catalysts mentioned are aluminium oxide, chromium oxide and silica-alumina. In the case of 2,6-xylenol, transalkylation with phenol, followed by isomerisation, can also be accomplished without a catalyst in the vapour phase at 550 – 600 °C or, batchwise, in the liquid phase at 420 - 470 °C [Fiege, 2003].

Tiwari and Mukherjee [1984] studied the effect of the ratio of phenol to higher methylphenols on transalkylation over a chromia-alumina catalyst. At a phenol : 2,6-xylenol molar ratio of 1:1, considerable amounts of trimethylphenols and isomerisation products were formed apart from cresols. At phenol : 2,6-xylenol molar ratios of 2:1 and 3:1 no trimethylphenols were formed but the formation of cresols and isomerisation still occurred. At a phenol : 2,6-xylenol molar ratio of 4.9:1, only cresols formed, while isomerisation did not occur anymore at all.

Tiwari and Mukherjee's results also showed increasing conversion of xylenols to cresols with increasing phenol : 2,6-xylenol ratio. From this it can be seen that increasing the ratio of phenol : higher methylphenols shifts the product distribution to smaller carbon numbers (lower methylphenols). This product distribution, while kinetically controlled, was explained by simple statistical reasons assuming that the extent of coverage of the catalyst surface by each of the individual reactants is proportional to the relative concentrations of the reactants (phenol and higher methylphenol) in the feed and that way determines the chance of a higher phenol molecule reacting with a phenol molecule or another methylphenol molecule.

At high conversion, the product mixture approaches thermodynamic equilibrium, with only the average number of side chains in the reaction mixture determining its equilibriun carbon number distribution.

2.5.4.1 Mechanism of phenols transalkylation

A broad spectrum of products, consisting mainly of cresols, xylenols, anisoles, methylanisoles and diphenyl ethers is obtained when phenol is methylated using zeolites [Hölderich and van Bekkum, 1991].

The same spectrum of products but without anisoles and methylanisoles can be expected in the case of transalkylation of phenol with higher methylphenols. Pierantozzi and Nordquist [1986] calculated that C-alkylation is thermodynamically favoured 10^4 times over O-alkylation (at 300°C), so no methyl ethers can form.

The transalkylation of phenol with higher methylphenols proceeds via a second order reaction. The mechanism shown in figure 2-7 is proposed for the transalkylation of phenol with higher methylphenols on acidic zeolite catalysts. It is based on a Rideal mechanism suggested by Santacesaria et al. [1990b] for phenol methylation, in which the one molecule is protonated and adsorbs on the Brønsted acid site as a carbenium ion while the second molecule approaches from the fluid phase.

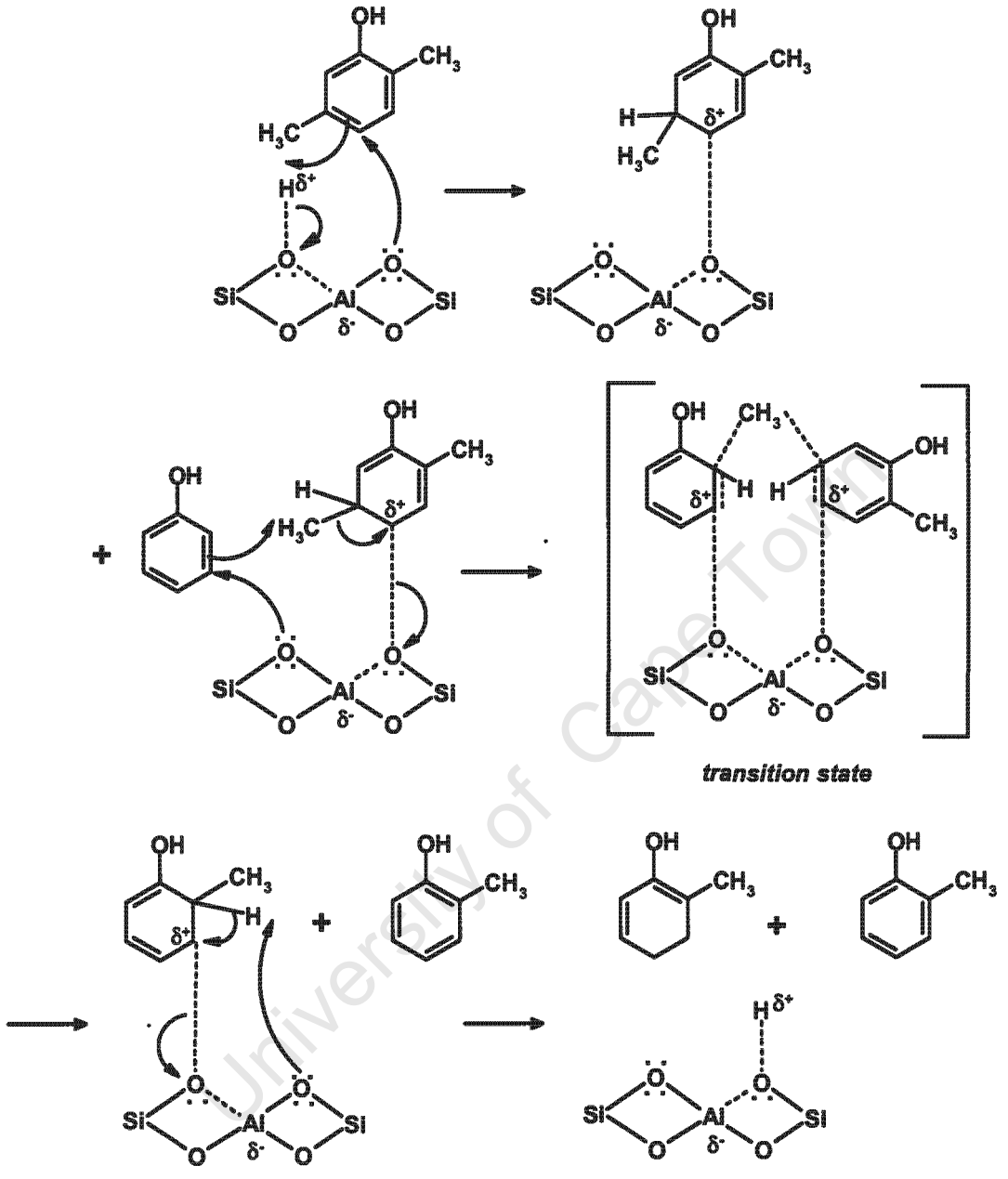


Figure 2-7: Mechanism of phenol transalkylation with a higher methylphenol on a zeolite Brønsted acid site [from Santacesaria's et al. Rideal mechanism of phenol methylation, 1990b, adapted, and Böhringer, 2006]

2.5.5 Selectivity of isomerisation and transalkylation

Selectivity of isomerisation and transalkylation is determined by various factors such as reaction conditions and catalyst activity and structure. Results obtained from preliminary experiments at UCT [Nyoni and Molefe, 2002] show that with increasing conversion there is an increase in the selectivity of transalkylation accompanied by a decreasing selectivity in isomerisation. These results are summarised in table 2-1.

Table 2-1: Isomerisation and transalkylation (disproportionation) of xylenol isomers under conditions of changing temperature and conversion over 6 g of H-ZSM5 in a fixed bed reactor at 36 bar and a space velocity of 0.2 h^{-1} [Nyoni and Molefe, 2002]

Feed	*T (°C)*	*Conversion (%)*	*Selectivity (%)*		*Yield (%)*	
			*Isom**	*Trans***	*Isom**	*Trans***
2,4-xylenol	250	2	100	0	2	0
	300	30	96	4	29	1
	350	74	69	31	51	23
2,6-xylenol	250	2	98	2	2	0
	300	3	75	25	2	1
	350	44	70	30	31	21
	400	76	40	60	30	46

* Isomerisation

**Transalkylation

Because isomerisation is a far more easy reaction than transalkylation in terms of activation energy and steric/geometrical requirements [Böhringer, 2006], it is expected that this reaction will happen much faster than the transalkylation reaction and dominate in the beginning. However isomerisation will reach equilibrium rapidly with increasing conversion. This will lead to more and more

transalkylation taking place. Isomerisation products will be increasingly consumed in the process by transalkylation and this leads eventually to decreasing amounts of the isomerisation products with increasing conversion [Böhringer, 2006].

It is expected that narrow pore zeolites will favour isomerisation over disproportionation because of the bulky intermediates required in the case of transalkylation. This has been shown by comparing zeolites H-ZSM-5 and H-USY as catalysts for cresol conversion [Imbert et al., 2000].

Decreasing catalyst activity (through deactivation) affects both isomerisation and transalkylation; however, transalkylation is affected more than isomerisation. Transalkylation requires stronger acid sites than isomerisation; hence deactivation affects the former reaction more than the latter. Coke deposition (resulting in deactivation) may also narrow pore diameters of the catalyst (or plug pores). This would also lead to isomerisation products being favoured [Imbert et al., 2000].

2.6 Ether formation

The formation of diphenylether is a common side reaction of acid catalysed reactions of phenolic compounds. For instance they form as a by-product during acid catalysed phenol methylation [Fiege, 2003]

The mechanism shown in figure 2-8 is proposed for the formation of diphenylethers during the transalkylation of phenol with higher methylphenols on acid zeolite catalysts.

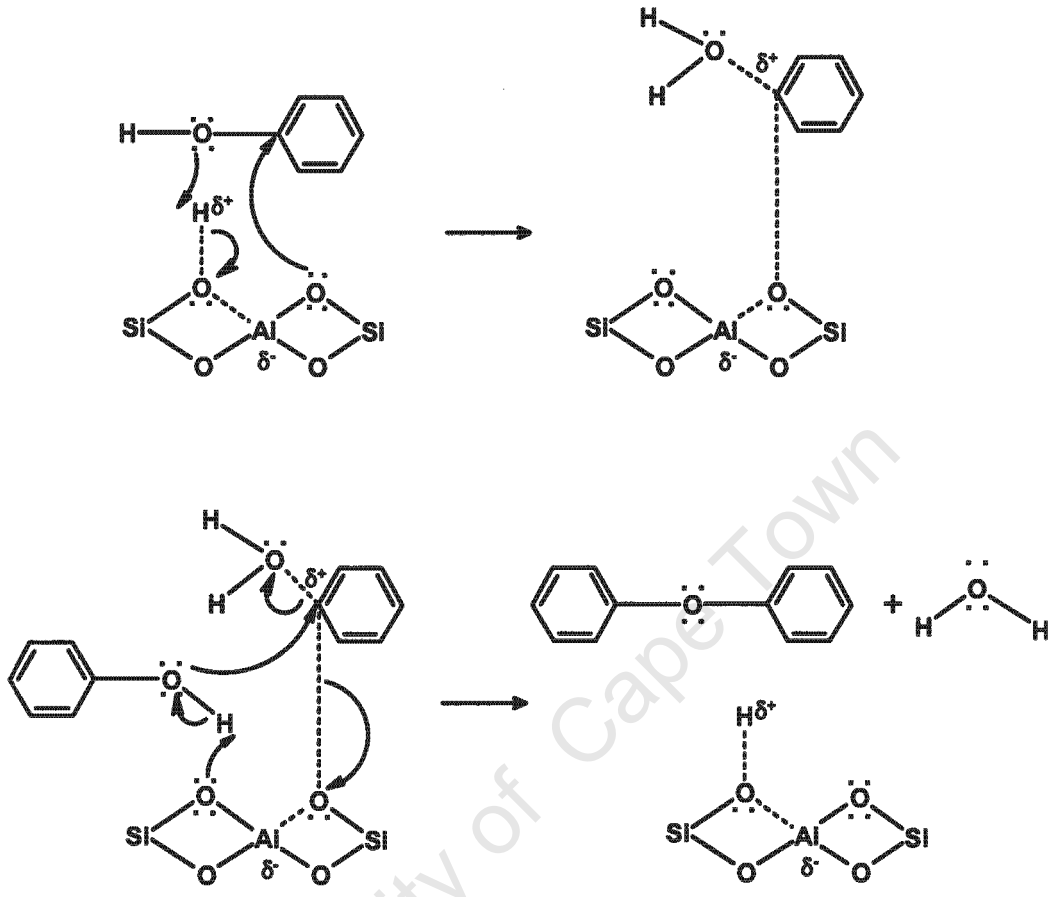


Figure 2-8: Possible mechanism for the formation of diphenylethers during phenol transalkylation with a higher methylphenol on a zeolite Brønsted acid site [from Santacesaria's et al. Rideal mechanism, 1990b, adapted, and Böhringer, 2006]. Possible alkyl substituents not indicated

2.7 Thermodynamics of phenolics transalkylation

2.7.1 Cresol isomers equilibrium distribution

The gas phase equilibrium distributions of the cresol isomers obtained experimentally by Imbert et al., at 380 °C over H-ZSM-5 (1997) and over H-USY (2000) and the liquid phase equilibrium distribution obtained by Fritsch et al. (2003), are shown in table 2-2.

Table 2-2: Cresol isomers gas and liquid phase equilibrium distributions (380°C) determined experimentally by Imbert et al. [1997] and [2000], and Fritsch et al. [2003]

	Distribution		
Isomer	*Gas phase*		*Liquid phase*
	Imbert et al., 1997	*Imbert et al., 2000*	*Fritsch et al., 2003*
p-Cresol	16	14	16
m-Cresol	48	44	48
o-Cresol	36	42	36

The distributions given in table 2-2 show that m-cresol is the thermodynamically favoured isomer. Imbert's et al. [1997] results at 380°C were confirmed by Fritsch et al. [2003] for liquid phase at the same temperature. Gas and liquid phase equilibrium being identical can be ascribed to the fact that, while not using any solvents, cresol isomers are surrounded by cresol isomers, i.e. individual activity coefficients, relative to each other, are very close to 1. Fernsby [2006] calculated the thermodynamic equilibrium distribution of the cresol isomers as a function of temperature from thermodynamic data from Stull et al. [1969], figure 2-9.

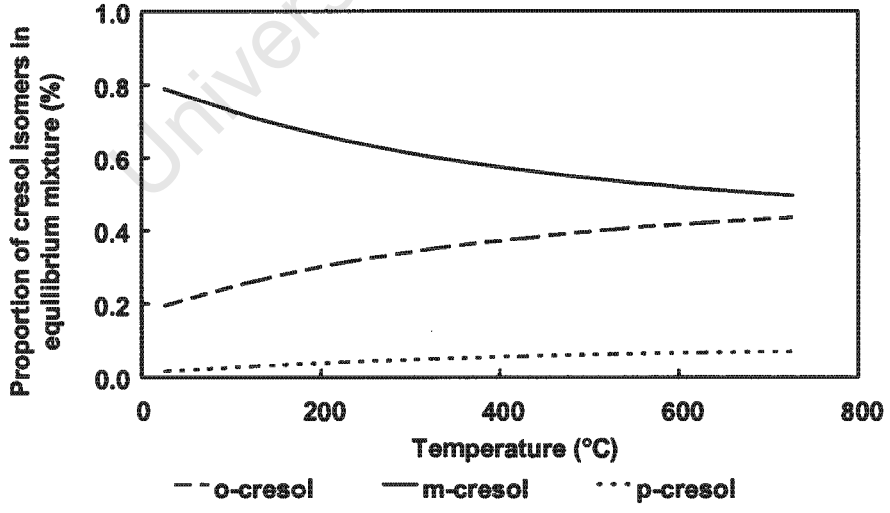


Figure 2-9: Thermodynamic equilibrium distribution of cresol isomers, calculated using thermodynamic data from Stull et al., 1969 [Fernsby, 2006]. It should be noted that Imbert et al. [1997] claimed that Stull's data for phenols are not very accurate

2.7.2 Xylenol isomers equilibrium distribution

The ideal gas phase xylenol isomers thermodynamic equilibrium distribution was measured by Pigman et al. [1954] and calculated by Fernsby [2006] using thermodynamic data from Daubert et al. [1999] is shown in table 2-3. Analogous to cresols equilibrium (section 2.7.1) it can be assumed that liquid phase equilibrium does not differ from gas phase equilibrium. According to these measurements and calculations, 2,4-Xylenol is the thermodynamically most stable isomer.

Table 2-3: Thermodynamic equilibrium distributions of xylenol isomers at different temperatures in ideal gas phase calculated using data from Daubert et al., 1999 [Fernsby, 2006] and measured by Pigman et al. [1954]

Isomer	*Xylenol isomers thermodynamic equilibrium distribution (%) at different temperatures (°C)*							
	Fernsby [2006]							*Pigman et al.* [1954]
	250	*275*	*300*	*325*	*350*	*375*	*400*	*344*
2,3-Xylenol	2.9	3.1	3.2	3.4	**3.6**	3.7	3.9	**8.9**
2,4-Xylenol	45.3	44.8	44.3	43.9	**43.5**	43.1	42.7	**29.6**
2,5-Xylenol	17.5	17.6	17.6	17.6	**17.7**	17.7	17.7	**23.7**
2,6-Xylenol	13.0	13.0	12.9	12.9	**12.9**	12.8	12.8	**11.1**
3,4-Xylenol	4.8	5.2	5.5	5.8	**6.1**	6.4	6.7	**12.6**
3,5-Xylenol	16.4	16.4	16.4	16.4	**16.3**	16.3	16.3	**14.1**

2.8 Uses of phenol, cresols and xylenols

Phenol, cresols and xylenols have wide applications. Some major applications are summarised in table 2-4.

Table 2-4: Major uses of phenol, cresols and xylenols [Fiege, 2003]

Phenol / Cresol isomer / Xylenol isomer	***Used for production of mainly, e.g.***
Phenol	formaldehyde resins bisphenol A which is an important starting material for polycarbonates and epoxy resins
o-Cresol	carvacrol which is used in antiseptics and fragrances
	o-crestonic acid which is used in dye intermediates and pharmaceuticals
	4-chloro-2-methylphenoxyactic acid, 2-(4-chloro-2-methylphenoxy)-propionic acid and γ-(4-chloro-2-methylphenoxy)-butyric acid, which are important as selective herbicides
p-Cresol	2,6-di-tert.-butyl-p-cresol (BHT) which is a nonstaining and light-resistant antioxidant with a wide range of applications
	2,6-nitro-p-cresol which is used as a polymerisation inhibitor in the production of styrene
m-Cresol	thymol, which is used in fragrances
	2,4,6-trinitro-m-cresol which is used in explosives
2,3-Xylenol	pesticides
2,4- / 2,5-Xylenol mixture	antioxidants
2,6-Xylenol	poly(phenylene oxide) resins
3,5-Xylenol	various pesticides, especially 3,5-dimethyl-4-methylthiophene
3,4-Xylenol	insecticide 3,4-dimethylphenyl methylcarbamate

2.9 Major sources of phenolic compounds

2.9.1 Isolation from coal tars and gasification liquors

A traditional source of phenol, cresols and xylenols is the high-temperature coke oven tar. This is obtained in the production of metallurgical coke by horizontal chamber coking of bituminous coal at 900 – 1300 °C. This tar contains, on

average, about 1.5 – 2 wt % phenol, cresols and xylenols (see table 2-5). However, coke oven tar has continuously been declining as a source of cresols and xylenols over the past 40 years [Fiege, 2003].

Cresols are also produced from the low temperature coal tars obtained in the production of smokeless fuels in the Coalite process that is operated in the UK [Fiege, 2003]. In these low temperature coal tars, the content of C_6 – C_8 phenols is about 10 times higher than in high-temperature tars (table 2-5a). By the 1990s Coalite tars had also become less abundantly available.

Tars from coal gasification in Lurgi gasifiers, that are produced at somewhat lower temperatures (by Sasol in South Africa and Dakota Gasification in the US), contain more phenols. Yields are given in table 2-5. Note the different bases of quantification in table 2-5.

The largest source of "natural" cresols and xylenols today is Sasol (producing 35 000 – 55 000 tonnes per annum). These cresols and xylenols are obtained from the liquid by-products of the steam gasification of bituminous coal by the Lurgi process to produce synthesis gas for the Fischer-Tropsch plants (see sections 2.9.3 and 2.9.4 for details of the Lurgi process and phenolic by-products recovery). The composition of the phenol fraction obtained from this process is similar to the composition obtained from low temperature coal tars [Fiege, 2003].

The largest, by volumes processed, of companies that isolate cresols and xylenols from coal tars are Sasol Phenolics in South Africa and Merichem in the United States, since 1997 in joint venture (named Merisol) and also in contract with Dakota Gasification in the United States for working up their phenolic streams [Fiege, 2003].

Table 2-5: Yields and distribution of phenols in tar acids from different processes [Gentry, 1928, and Fiege, 2003]. Note the different bases (either the tars or the coal itself) for calculations

Constituent	Amount		Yield		
	(wt % of total tar)	(% of total tar)*	(wt % of coal)		
	High temperature coke oven tar [Fiege, 2003]	Low temperature Coalite process tar acids [Gentry, 1928]	Lurgi gasifier tar***		
			Bituminous coal [Fiege, 2003]		Lignite [Fiege, 2003]
			600 – 650°C	800 – 900°C	
Phenol	0.4 - 0.6	0.11	0.14	0.014	0.61
Cresols	0.8 – 1.0	4.78	0.31	0.063	0.5
Xylenols	0.2 – 0.5	5.88	0.61	0.078	0.3
Higher phenols	-	7.07	1.24	0.167	-
Total phenols**	**17.8**	-	**2.30**	**0.322**	-

*Assumed to be weight percentage

**The remainder is composed of the heavier derivatives of phenol, resins etc.

***Data given in kg/ton of coal in Fiege [2003] but converted to weight percentage in this table

2.9.2 Recovery from refinery caustics

"Natural" cresols and xylenols are also obtained from the naphtha fractions produced by catalytic and thermal cracking in the petroleum industry in the United States. These naphtha fractions contain on average about 0.1 % $C_6 - C_8$ phenols. The phenols in these naphtha fractions are extracted as a by-product in a process called sweetening where scrubbing of acid sulphur compounds (e.g. thiols) is done with concentrated alkaline solutions. This treatment removes phenols as well. The spent refinery caustics contain on average 20 – 25 % $C_6 - C_8$ phenols and 10 – 15 % sulphur compounds. A typical composition of the phenols fraction obtained from spent refinery caustics is shown in table 2-6 [Fiege, 2003].

Table 2-6: Typical composition (wt %) of the phenols fraction obtained from spent refinery caustics

Phenol	*o-Cresol*	*m-Cresol*	*p-Cresol*	*Xylenols**	*Higher phenols*
20 %	18 %	22 %	9 %	28 %	3 %

*Includes ethylphenols

The recovery of cresols and xylenols from spent refinery caustics has so far been confined to the United States. Recovery from spent refinery caustics is declining due to the fact that refineries are changing the desulphurisation of their naphtha fractions to processes like hydrotreating and the Merox process from which substantial quantities of phenolics remain in the gasoline and considerably smaller amounts of spent caustics are obtained [Fiege, 2003]. Competition from synthetic producers of o-cresol, increased environmental restrictions and an overall lack of raw material, forced competitors to close down their operations so that since around 1990 Merichem is the only processor of spent refinery caustics in the United States [Fiege, 2003].

In 1996, the "cresylics" capacity of Merichem was about 55 000 tonnes per annum. This quantity includes phenol, xylenols and several other alkylphenols. Merichem, now with their phenolics business in joint venture "Merisol" with Sasol Phenolics isolate cresols not exclusively from spent refinery caustics but also from a variety of sources such as the coal gasification plants of Dakota Gasification and Sasol [Fiege, 2003].

2.9.3 The Lurgi coal gasification process

Coal is first washed, crushed, graded and then fed from the top into the gas producer from where it is slowly gravitating downwards. Gasification is carried out at about 30 bar with a mixture of oxygen and steam as co-feed which is blown into the reactor from the bottom, countercurrently to the coal, through a revolving grate. A bed of ash resting on the grate preheats and distributes the gasifying medium evenly.

The gasifying medium is heated by combustion of the ungasified rest of the coal with the oxygen in a shallow combustion zone. This is followed, upwards, by a zone in which mainly gasification by steam occurs. In the next layer the coal is devolatised and gasified by hydrogenation. The raw gas leaving the gasifier dries and preheats the fresh coal. The raw gas produced leaves the gasifier at a temperature of between 300 – 800 °C depending on the type of coal used. Ash is periodically removed from the base of the gasifier [Schilling et al., 1981].

The raw gas is then quenched with water to 180 – 200 °C in a scrubber cooler and eventually cooled to ambient temperature where the gas liquor, raw naphtha, oil and tars condense out [Schilling et al., 1981], see figure 1-1.

2.9.4 Recovery of phenolics from Lurgi coal gasification process tars and liquors

Many processes have been developed for the recovery of phenolic compounds from aqueous process streams, however, the most widely applied process in industry is the Phenosolvan process (section 2.9.4.1).

A commercially feasible process is under development (but not yet operating) for the recovery of phenolic compounds from the naphtha fraction from the organic phase of the gasifier product condensate and coal tars (section 2.9.4.2).

2.9.4.1 Phenosolvan process

The design of the Phenosolvan process is rather simple. In the Phenosolvan process, the filtered and neutralised aqueous stream from the Lurgi gasification process (the gasification liquor) is treated countercurrently with a suitable solvent in a multistage extractor. The extract is separated in a distillation column into a pure solvent (overhead product) and a crude phenols (bottoms product) stream. The solvent is recycled to the extractor. The small amount of solvent that remains in the phenolic raffinate is removed by stripping [Stönner, 1989].

Different feedstocks can be treated and different solvents or solvent mixtures can be used for the Phenosolvan process. Examples of suitable solvents are butylacetate, diisopropylether (DIPE), mixtures of benzene and DIPE or mixtures of methyl isobutyl ketone (MIBK) and DIPE [Stönner, 1989].

A typical composition of a (depitched) Phenosolvan extract from steam gasification of coal is shown in table 2-7 [Stönner, 1989]. It should be noticed that this extract reflects only a part of the total phenolics produced in the coal gasification process (see table 2-5 for the total distribution) and is dominated by

the lower phenolics that appear in the aqueous phase, the liquor, with preference.

Table 2-7: Typical composition of a depitched Phenosolvan extract from the liquors from steam gasification of coal [Stönner, 1989]

Compound	*Weight Percentage*
Phenol	45
Cresols	30
Xylenols	6
Polyhydric and other phenols	10
Pyridine bases	1
Neutral oil, pitch	5
Water	3

2.9.4.2 Separation of phenolic compounds from neutral oils and nitrogen bases.

Venter and Nieuwoudt (2002) have developed a process (Nieuwoudt and Venter, 1998) for the recovery of phenolics from the naphtha fraction of coal tars (figure 2-10). Further development of this process is currently taking place in industry. It is a liquid-liquid extraction process with a solvent stream consisting of triethylene glycol and water and a countersolvent stream consisting of n-hexane.

The feed to the extractor consists of a mixture of phenolic compounds, neutral oils and nitrogen bases in the heavy naphtha range. The solvent stream enters the extraction column at the top together with the feed stream, while the countersolvent stream enters at the bottom. The constituents of the feed stream are distributed between the two phases by means of countercurrent extraction, with the raffinate and extract phases exiting at the top and bottom of the column, respectively [Venter, 2001].

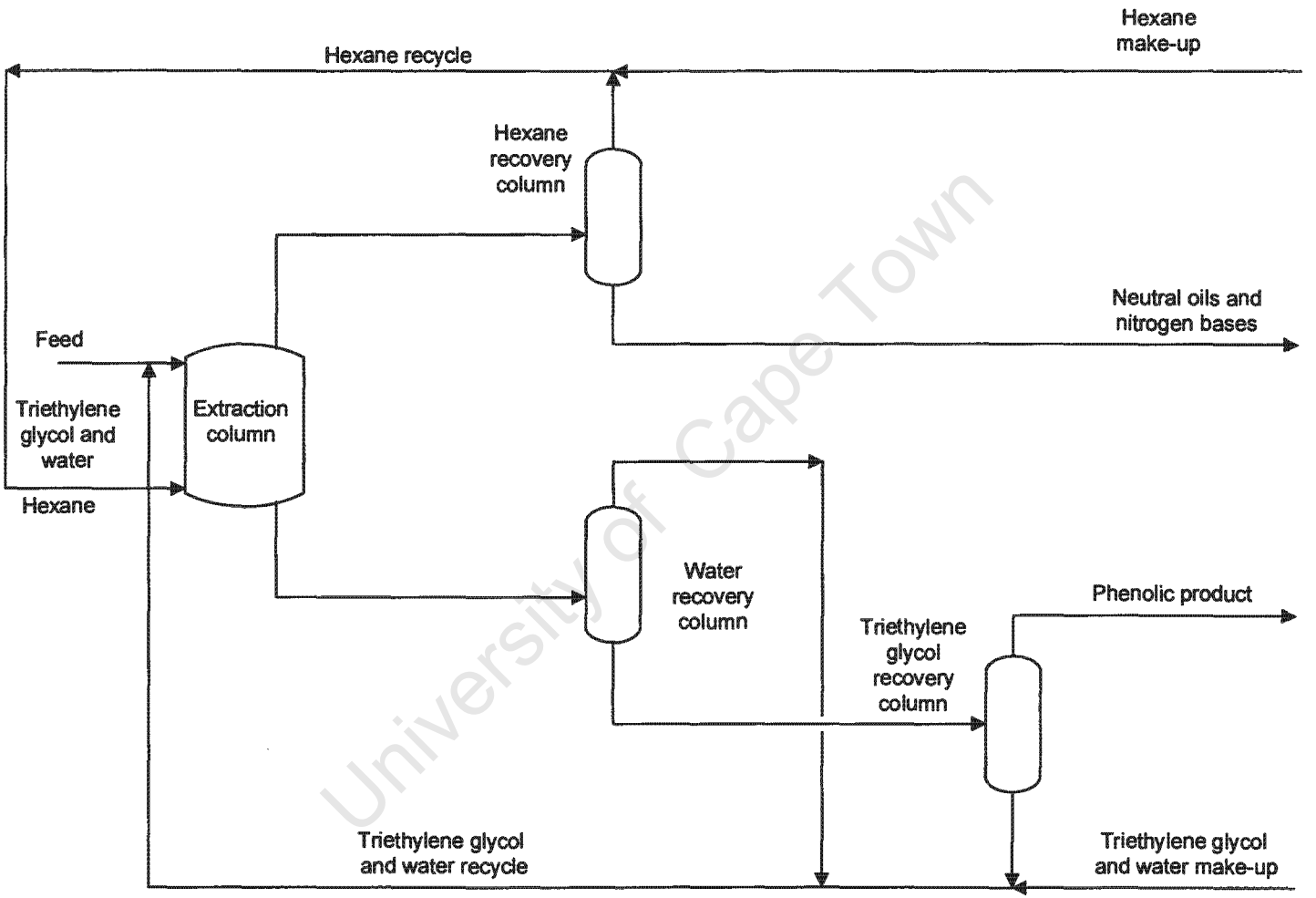


Figure 2-10: Process flow diagram for the recovery of phenolics from the naphtha fraction of coal tars [Venter, 2001], simplified

The countersolvent phase exiting the column at the top consists of hexane, the neutral oils, nitrogen bases and traces of phenolic compounds, water and triethylene glycol. This exiting stream is sent to a hexane recovery unit where hexane and any water present are removed yielding a high purity hexane with respect to neutral oils and nitrogen bases. It is not necessary to remove the residual water in the hexane distillate as both hexane and water are ultimately recycled to the extraction column [Venter, 2001].

The solvent phase exiting the column at the bottom consists of triethylene glycol, water, the bulk of the phenolic compounds from the original feed mixture and traces of neutral oils, nitrogen bases and hexane. This exiting stream is fed to a water recovery column where water and any residual hexane are removed.

A number of neutral oils and nitrogen bases form azeotropes with water and a substantial percentage of the traces that remained in the solvent phase compounds are thus removed with the water. Azeotropic removal of phenolic compounds with the distillate is prevented due to the formation of hydrogen bonding between the phenolic compounds and the triethylene glycol present in the extract. As a result only a very small fraction of phenolic compounds, compared to neutral oils and nitrogen bases, is removed azeotropically [Venter, 2001].

The phenolic compounds and triethylene glycol, and the traces of neutral oils and nitrogen bases that are still present in the extract phase, are recovered as a bottoms product of the water recovery column. This product is fed to a solvent recovery column from which the phenolic compounds, along with any residual neutral oils, nitrogen bases and water are removed as distillates. This distillate stream is the final (raw) phenolic product stream. Triethylene glycol is recovered as the bottoms product and is recycled to the extraction column [Venter, 2001].

The process was found to be capable of processing a raw heavy naphtha feed with a boiling range of 160 to 220 °C and a phenolic product purity in excess of 99.5% being obtained. The author claims that separation is achieved with reasonable solvent to feed ratios and in few separation steps with low solvent losses [Venter, 2001].

No data are published yet about the composition of the phenolics fraction obtained from the heavy naphtha stream of a Lurgi coal gasifier using the new process. However, given the proportions of a gasifier naphtha (organic) compared to the gasifier liquor (aqueous), with the former being non-protonic and less polar, it can be assumed that the carbon number distribution of the phenolic extract from the naphtha tends significantly to the phenolic compounds with more and longer alkyl side chains, i.e. the higher phenols, though limited to ca. C_9, corresponding to the higher boiling end of the naphtha.

With Sasol's plannings to extract the phenolic fraction from the raw gasifier naphtha (du Preez, 2003) not only more phenol, cresols and xylenols, but also significantly more of the low value higher phenols (particularly C_9 phenols) will thus be available.

However, it is not known yet whether Sasol's process will be identical with or similar to the Venter / Nieuwoudt process or not.

2.10 Zeolites

2.10.1 What are zeolites?

Zeolites are microporous crystalline solids with well defined pore structures. They generally contain silicon, aluminum, oxygen, cations, water and/or other molecules in their framework [Bell, 2001]. They occur naturally and are also

synthetically produced. Typically, a zeolite framework is composed of tetrahedrally co-ordinated silicon atoms (T-atoms) joined by oxygen atoms.

Substitution of some of the T-atoms with other atoms (e.g. Al, P etc.) is common and desired. The main feature of a zeolite framework is the presence of micro pores. Some frameworks have one-dimensional pores; some have pores extending in two or three dimensions which can join at pore crossings or even cage-like intersections. Substitution into the framework, Al for Si for example, creates areas of excess negative charge where non-framework species can bind [Deem, no year].

2.10.2 What makes zeolites special?

What makes zeolites special is (i) the microporous pore character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting others, based on too large a molecular size, (ii) the ion exchange properties which allow to perform many different ion exchange reactions, (iii) the ability to develop internal acidity which enables zeolites to catalyse organic reactions and (iv) the high thermal stability [Moscou, 1991].

Zeolites can be used to directly synthesize compounds that are essentially free from unwanted by-products. As heterogeneous catalysts, they posses the usual advantages over homogeneous catalysts i.e. they are easy to separate from products, easy to handle and easy to regenerate. Zeolites offer an ability to control catalytic properties by a variety of synthetic and post synthetic methods. Pore size and shape can be influenced by choosing the appropriate organic template and synthesis conditions i.e. making different types of zeolites. Acidity of zeolites can be also be controlled by various methods such as the degree of substitution of the silicon by e.g. aluminium atoms, i.e., the silica/alumina ratio, ion exchange and calcinations conditions [Davis et al., 1994].

Most of the important reactions carried out over zeolites are acid-catalyzed. However there is an increasing interest in zeolite catalysis by basic sites [Karge, 1991].

2.10.3 Generation of acid sites

Acidity of zeolites could mean (i) the nature of acidic sites (Brønsted sites or Lewis sites), (ii) number or density of the sites or, finally (iii) their strength [Karge, 1991]. As mentioned above, the substitution of Si in the zeolite lattice with Al results in excess negative charge. This excess negative charge is compensated for by cations. Brønsted acid sites (proton donors) are formed when the charge compensating cation is a proton. This can be achieved by one of the following processes, (i) ion exchange of the charge compensating cations with protons in a liquid Brønsted acidic medium, (ii) ion exchange with ammonium ions, followed by an activation step (usually thermal) whereby ammonia is expelled, (iii) calcination whereby organic structuring cations are thermally decomposed, (iv) hydrolysis of hydration water by polyvalent cations and (v) reduction of cations to a lower valence state. These processes lead to formation of bridging hydroxyls (proton donor sites) which are the locus of Brønsted acidity and catalytic activity in proton aluminosilicate zeolites (see figure 2-11). Theoretically, one Brønsted acid site can be generated for each aluminum in the framework, hence the larger the aluminum content or the lower the Si:Al ratio of a zeolite, the larger the potential number of Brønsted acid sites [Martens et al., 1997].

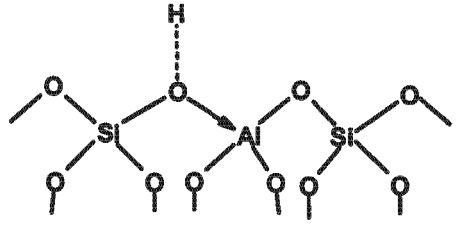
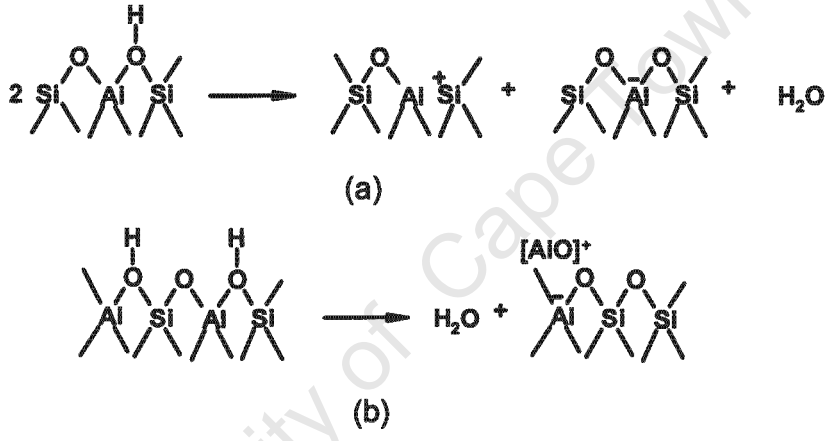


Figure 2-11: Bridging hydroxyl group in aluminosilicate zeolite generating Brønsted acidity [Martens et al., 1997]

The free electron pairs on the oxygen on the opposite site of the aluminium atom act as an electron donor site, i.e., a Lewis base [Martens et al., 1997], thus contributing to the acid catalysed reactions in a concerted manner as shown, for example, in figures 2-7 and 2-8.

A Lewis acid site (electron pair acceptor) is generated upon dehydroxylation of two Brønsted acid sites (figure 2-12(a)). Lewis acid sites in the form of extra-framework AlO^+ species can be formed during dehydroxylation of two adjacent Brønsted acid sites (see figure 2-12(b)) [Jacobs et al., 1979].



Figures 2-12(a) and (b): Formation of a Lewis acid site from two Brønsted acid sites [Jacobs et al., 1979]

For the majority of the acid-catalyzed reactions, the relevant acid sites are the Brønsted acid sites [Karge, 1991].

2.10.4 Acid site sensity

The overall density of Brønsted and Lewis acid sites in a zeolite can be determined by chemisorption of basic probe molecules and quantification of the adsorbed molecules. This is done by saturating a zeolite sample with a strong basic molecule and then evacuating the physisorbed molecules after which the

chemisorbed molecules are removed with a flow of an inert carrier gas during a temperature programmed desorption process [Martens et al., 1997].

It is usually observed that with carefully prepared, high Si : Al ratio zeolites, the number of acid sites is proportional to the aluminum content [Herreros, 1996].

2.10.5 Acid site strength

Acid site strength distribution in zeolites can be determined by indirect methods, also using probe molecules. A few examples of these methods are (i) calorimetry, where the heat of adsorption of basic probe molecules is measured, (ii) temperature programmed desorption combined with selective spectroscopy, a method where pyridine is used as the spectroscopic probe, and (iii) IR spectroscopy where weaker bases such as benzene, ethylene and carbon monoxide are used as spectroscopic probes [Martens et al., 1997]. The stronger acid sites are usually observed in high Si : Al ratio zeolites.

2.11 Shape selectivity in zeolites

Almost any thermodynamically possible chemical reaction may occur to some extent at a sufficiently high temperature. It follows that the most unique role and purpose of a catalyst is to provide a selectivity to direct the transformation along a very specific, desired path [Weisz, 1980]. There are various methods of achieving certain selectivities in zeolites, some of which depend on the relative rate of intracrystalline diffusion, while others do not. The most common types of shape selectivity are termed reactant, product and transition state shape selectivity. A first basic description of these effects was given by Csicsery [1984].

2.11.1 Reactant shape selectivity

This type of shape selectivity occurs when the feedstock consists of two types of molecules, those that are too big to enter the zeolite channel system and those that can enter the channel system. Reactant shape selectivity (figure 2-13) has been demonstrated, for instance, by the selective dehydration of n-butanol in a C_4-alcohol mixture over a calcium exchanged zeolite A (5A molecular sieve) without reacting isobutanol or secondary butanol [Weisz et al., 1962].

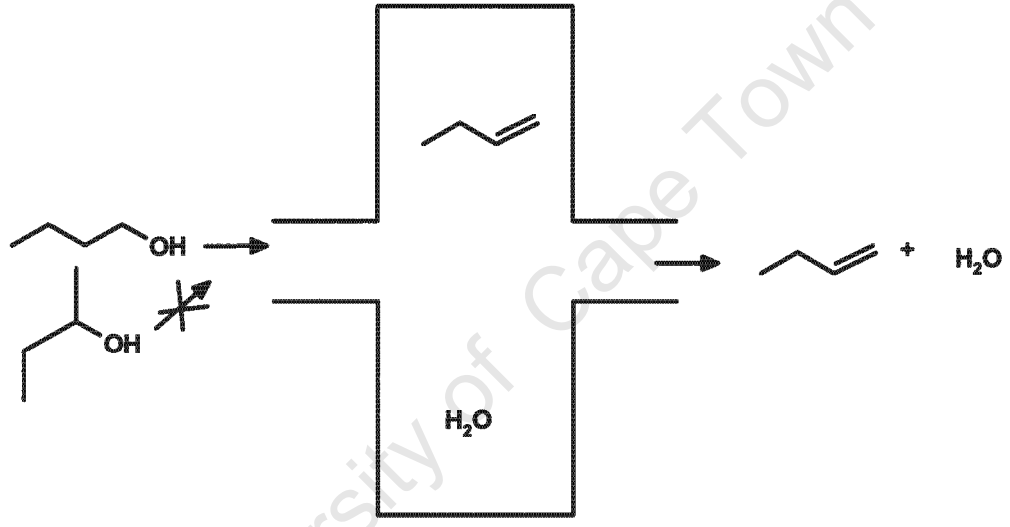


Figure 2-13: Reactant selectivity

2.11.2 Product shape selectivity

This type of shape selectivity takes place when the feed molecules can enter the pores of a zeolite and are converted into products, but when only some of the products formed are able to leave the zeolite cavities while others are trapped in the zeolite cavities due to them not fitting in the channels. These larger molecules remain in the pores getting accumulated or undergo secondary reactions like isomerisation into smaller products which then escape the zeolite cavities [Chen et al., 1994]. When approaching chemical equilibrium with the smaller ones, the larger molecules may slow down the reaction or sometimes, if not readily

converted into smaller molecules, deactivate the zeolite by fouling [Chen et al., 1994].

This type of shape selectivity was shown in the hydrogenation of an ethene and propene mixture over a platinum catalyst encapsulated in a small pore Na-mordenite. Both reactants can pass through the zeolite, but one of the products, propane, cannot get out again. As the result of this product selectivity only ethene was hydrogenated [Chen et al., 1994]. Product shape selectivity was also shown in shape selective toluene disproportionation to benzene and mainly p-xylene, the slimmest xylene isomer, over medium pore size zeolite H-ZSM-5 [Olson and Haag, 1984]. An illustration of product shape selectivity is given in figure 2-14.

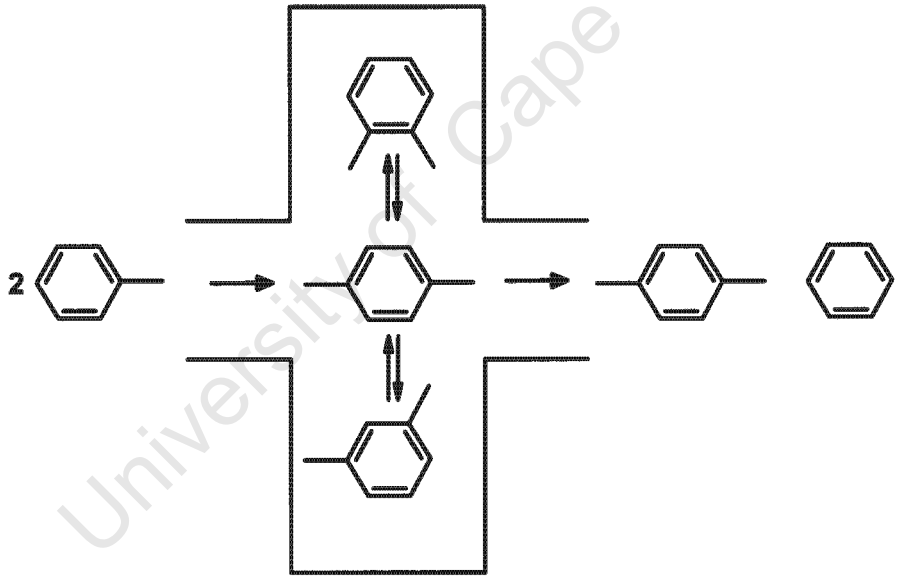


Figure 2-14: Product selectivity

2.11.3 Transition state selectivity

This type of selectivity takes place when both the reactant and the product molecules are small enough to travel through the zeolite channels, but the reaction intermediates or transition states of the reaction are spatially constrained

within the zeolite pores either by size or orientation [Chen et al., 1994]. This type of shape selectivity was also described by Csicsery [1971]. Csicsery observed the absence of symmetrical trialkylbenzenes in disproportionation product mixtures of dialkylbenzenes over H-mordenite (see figure 2-15). His reasoning for this was that some of the bimolecular disproportionation reactions would be inhibited due to them involving bigger diphenylmethane-type intermediates than others, which require more space than is available in the mordenite channels.

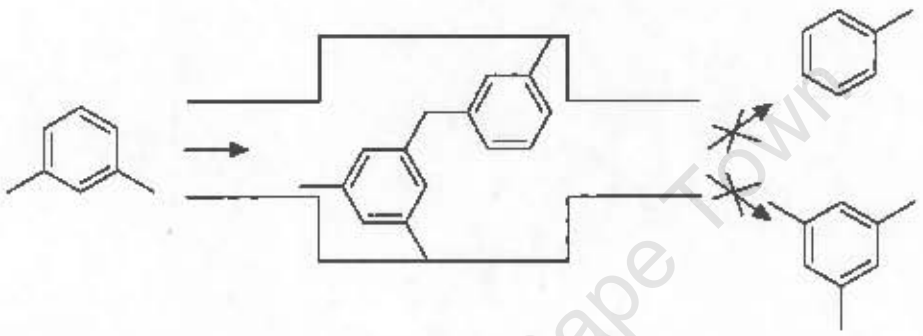


Figure 2-15: Transition state selectivity

2.12 Physical properties of the applied zeolites

2.12.1 Zeolite Beta (BEA)

Zeolite Beta has a three-dimensional pore system that consists of 12-membered rings [Treacy and Newsam, 1988, and IZA, 2002]. The framework of zeolite Beta is a randomly intergrown hybrid of two distinct but closely related structures [Treacy and Nowsam, 1988].

Zeolite Beta's pore system consists of two perpendicular systems of 12-membered ring straight channels of 6.6 x 6.7 Å (figure 2-16) that intersect with each other and also intersect, at the intersection of the two other channels, at right angles, with 12-membered ring sinusoidal channels of 5.6 x 5.6 Å that extend into the third dimension. The chemical formula of the sodium form of zeolite Beta is given by: Na_n $[Al_nSi_{64-n}$ $O_{128}]$ where $n \leq 7$. The SiO_2/Al_2O_3 molar

ratios are ≥ 16. The framework density is 15.1 T atoms per 1000 $Å^3$ [Baerlocher et al., 2001].

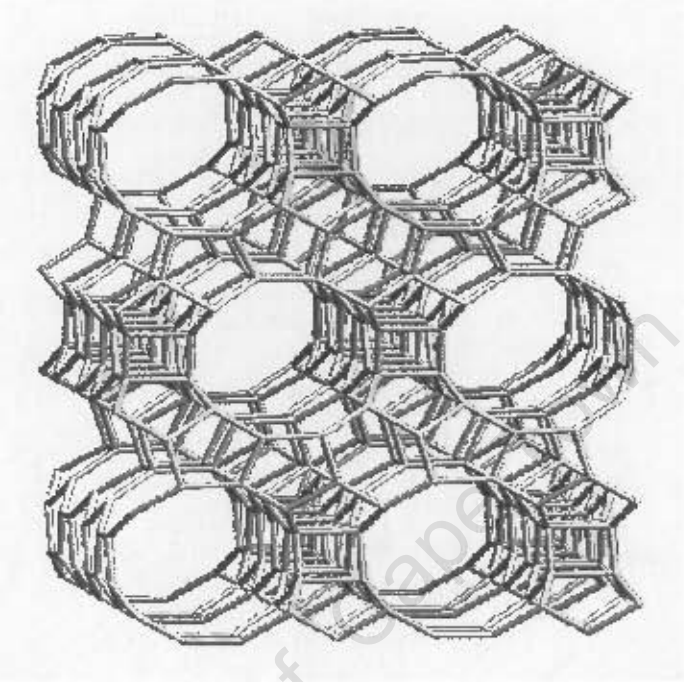


Figure 2-16: Framework structure of zeolite Beta (BEA) showing the straight channel [IZA, 2002]

2.12.2 Zeolite ZSM-5 (MFI)

The framework of zeolite ZSM-5 has a two-dimensional pore system consisting of 10-membered rings that form straight channels of 5.3 x 5.6 Å (see figure 2-17) intersecting at right angles with sinusoidal channels of 5.1 x 5.6 Å. Since the intersecting sinusoidal channels connect between neighboring straight channels, the pore system, with respect to molecular diffusion, is effectively three dimensional.

The chemical formula of the sodium form of zeolite ZSM-5 is given by: $Na_n (H_2O)_{16} [Al_nSi_{96-n} O_{192}]$ where $n \leq 8$. The SiO_2/Al_2O_3 molar ratios are ≥ 22. The framework density is 17.9 T atoms per 1000 $Å^3$ [Baerlocher et al., 2001].

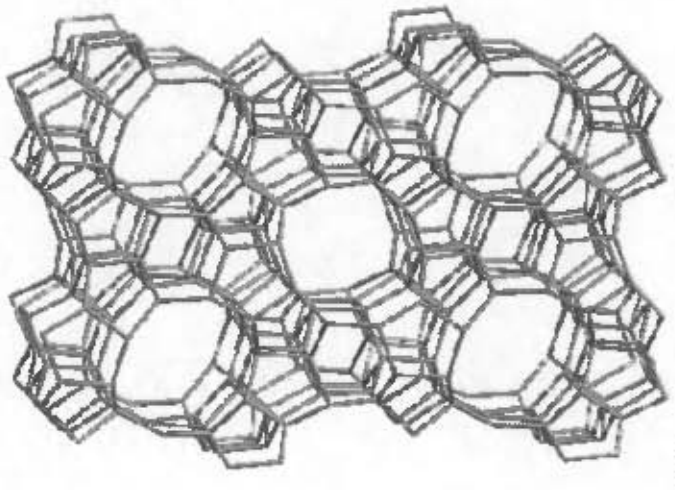


Figure 2-17: Framework structure of zeolite ZSM-5 (MFI) showing the straight channel [IZA, 2002]

2.12.3 Zeolite Mordenite (MOR)

The pore system in zeolite mordenite consists of two types of parallel channels. These are 8-membered ring channels of 2.6 x 5.7 Å and 12 membered ring channels of 6.5 x 7.0 Å diameter. These parallel channels are interlinked by 8-membered ring sinusoidal channels of 3.4 x 4.8 Å. At least for the diffusion of large molecules e.g. aromatics, mordenite has effectively only a single one-dimensional channel system, namely, the one made up of the 12 ring channels (see figure 2-18).

Mordenite occurs as a natural or synthetic zeolite and it is one of the most siliceous natural zeolites, the chemical formula of the sodium form is given by: $Na_n\ (H_2O)_{24}\ [Al_nSi_{40-n}\ O_{96}]$ where $n \leq 8$. The SiO_2/Al_2O_3 molar ratios are ≥ 10. The framework density of zeolite mordenite is 17.2 T atoms per 1000 $Å^3$ [Baerlocher et al., 2001].

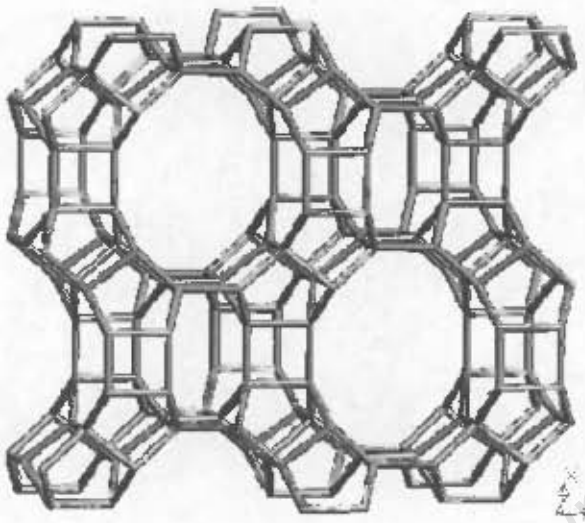


Figure 2-18: Framework structure of zeolite mordenite (MOR) showing the wide and (in between) the narrow straight channels [IZA, 2002]

Chapter 3

OBJECTIVE AND MOTIVATION

The objective in this research project was to convert polymethylphenols (C_{9+}) to cresols and xylenols. This was done by transalkylation of such higher phenols with excess phenol over acid zeolite catalysts. Initially a C_8-phenol, 2,5-xylenol was used as a model compound for basic studies and reasons of simplicity. Higher phenols such as a trimethylphenol isomer and a mixture of polymethylphenols C_{9+} were also used.

The motivation behind this project is the fact that cresols and xylenols have more applications and the more specific applications and thus significantly higher value than higher, polyalkylated phenols in particular when they are obtained as isomer mixtures. Sasol, South Africa's big producer of natural phenolics recovers such higher phenol mixtures, unavoidably, as a by-product in the aqueous and raw naphtha by-product streams of their Lurgi coal gasification process when applying the Phenosolvan liquor extraction and, as planned, the novel naphtha extraction processes.

This study was carried out to investigate a way of extracting additional value out of these higher phenols, converting them with phenol to cresols and xylenols. This would comprise recovery of the valuable aromatic (phenolic) OH-groups present in the constituents of the C_{9+}-phenolics fractions and also make use of the C_{9+}-polymethylphenols as an active – and cheap – reagent for the methylation of the phenol, due to the activation of their aromatic rings by the OH-group.

3.1 Reaction under study

The reaction under study was the transalkylation of phenol with polymethylphenols C_{8+} to produce lower methylphenols, namely cresols and

xylenols. This involved transfer of methyl groups from the polymethylphenol molecules to phenol molecules resulting in the production of lower methylphenols than the fed polymethylphenols and higher ones than the phenol. This can be exemplified with phenol and e.g. a trimethylphenol in the following reaction equation (figure 3-1).

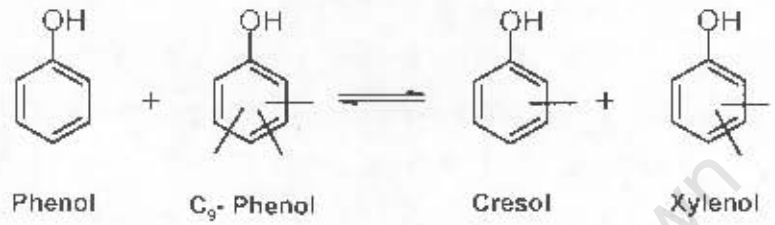


Figure 3-1: Equation of an example of the reactions under study

Reactions were carried out over acid zeolite catalysts. Zeolites have been chosen mainly because of their high and rather stable activity compared to amorphous materials such as silica-alumina. Medium pore and wide pore zeolites have been tested, the former in order to investigate if any shape selective effects can be introduced.

3.2 Expected product distribution

Transalkylating trimethylphenol with phenol in e.g. a 1:1 molar mixture was expected to lead to a rather symmetric carbon number distribution containing more cresol and xylenol product than remaining feed compounds phenol and trimethylphenol such as illustrated in figure 3-2. Note that the average carbon number, 7.5, does not change.

In fact, since transmethylation reactions between the polymethylated compounds in the reaction mixture would also form tertramethylated compounds and pentamethyl phenol, the carbon number distribution would be skew, as illustrated in figure 3-3. Note that the average carbon number still remains to be 7.5.

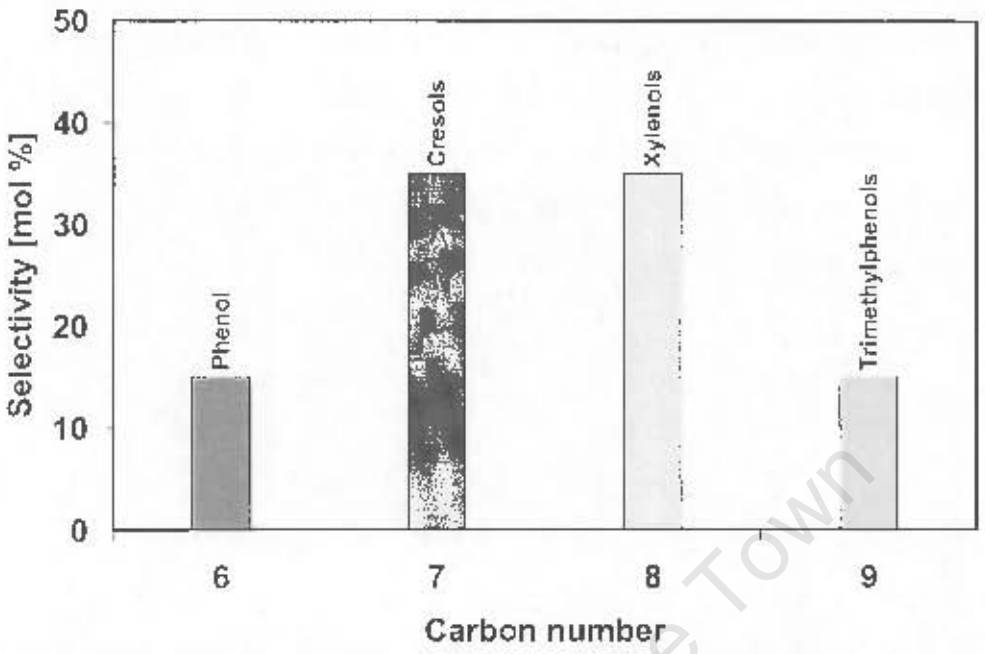


Figure 3-2: Expected carbon number distribution (approximate values) of the transalkylation product of a 1:1 molar mixture of phenol and trimethylphenol

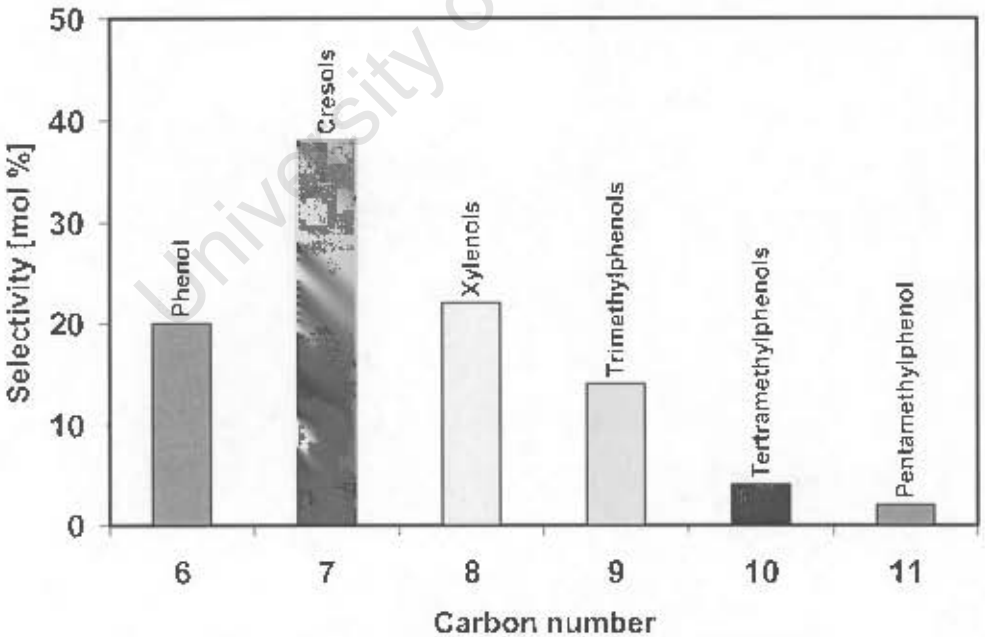


Figure 3-3: Expected carbon number distribution (approximate values) of the transalkylation product of a 1:1 molar mixture of phenol and trimethylphenol considering the formation of higher methylated phenols

Feeding excess phenol e.g. in a 5:1 molar ratio was expected to result in higher "dilution" of the methyl substituents, i.e. mostly cresols forming, consuming the most of the trimethylphenol and forming practically no higher methylated products, as illustrated in figure 3-4, which more or less, represents the expected product mixture, consisting eventually of phenol, cresols and some xylenols. Note that the average carbon number in this mixture is 6.5.

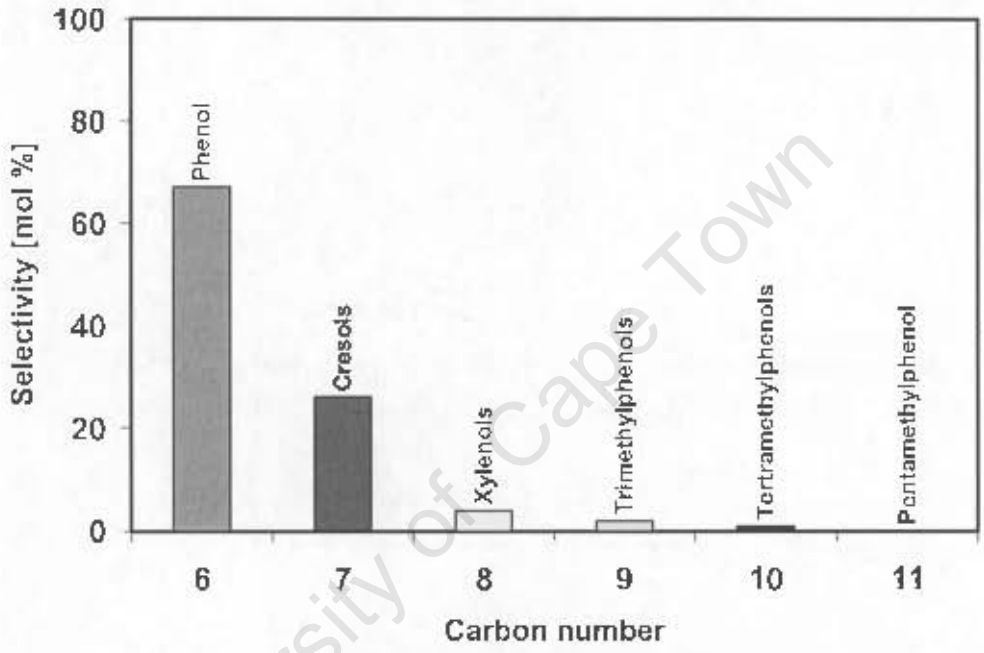


Figure 3-4: Expected carbon number distribution (approximate values) of the transalkylation product of a 5:1 molar mixture of phenol and trimethylphenol

3.3 Hypothesis

Low value polymethylated phenolic compounds (C_{9+} phenols) can be transalkylated with phenol to produce high value mono- and di-methylated phenolic compounds (cresols and xylenols).

3.4 Key questions

- Are acid zeolite catalysts suitable?
- Which commercially available zeolite catalyst is most suitable?
- Can the process be operated at attractively high rates, conversions and space velocities with low catalyst coking?
- Can the reaction be driven towards thermodynamic equilibrium carbon number distribution with low selectivity towards undesired by-products?
- Does the presence of higher methylated phenols in the reaction mixture suppress the net formation of higher transalkylation products?

Chapter 4

EXPERIMENTAL

4.1 Experimental setup

An experimental apparatus was built for the transalkylation reaction of phenol with 2,5-xylenol and higher phenols at high temperature and pressure in liquid phase. A flow diagram of the experimental set up is shown in figure 4-1. The experimental set up consisted of the following major units; feed pot, feed pump, reactor and product catch pot. Auxiliary parts comprised emergency and guard catch pots, pressure indicators (PI) and pressure indicator controllers (PIC), band heaters and heating lines, temperature indicators (TI) and temperature indicator controllers (TIC), mass flow controllers (FIC), filters (F), valves (V), safety valves (SV) and check valves (CV). Connection between the different units was done by 1/8 inch (for liquid carrying lines) and ¼ inch (for gas / vapour carrying lines) stainless steel tubes.

4.1.1 Mass flow controller and gas inlet filter

There was an inlet line to the experimental setup, for high pressure nitrogen gas (80 bar house-line supply pressure). Connected to this line were a pressure indicator and controller (PIC-113) and a Brooks thermal mass flow controller (FIC-122) of a flow range of 0 - 500 sccm. The calibration of this mass flow controller is shown in appendix B. The line to the pressure controller / mass flow controller set up was fitted with a filter (F-111) to protect the mass flow controller from dust.

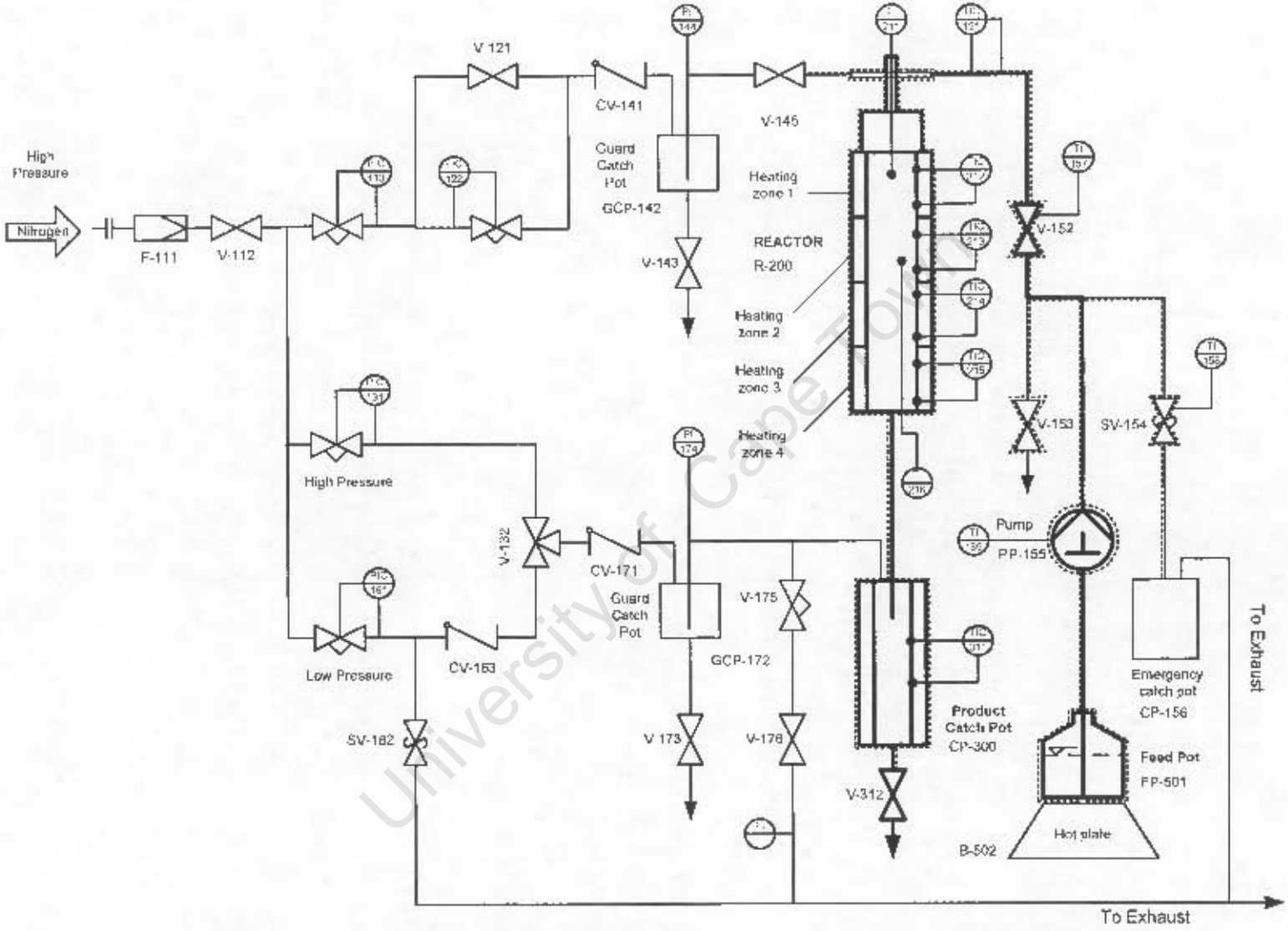


Figure 4-1: Flowsheet of the experimental apparatus (====== heated parts and lines)

4.1.2 Pressure regulation parts

For setting and maintaining a constant reaction pressure, the experimental setup was equipped with pressure indicator controllers, pressure indicators, pressure relief valves and a throttle valve. Pressure indicator controllers were used to set the desired gas pressures in the experimental setup. Pressure indicators were used to measure and indicate pressure at various points in the experimental setup.

Nitrogen was used for pressurising and maintaining the pressure in the experimental setup. Pressurising was done via the by-pass valve (V-121) and maintaining the reaction pressure was done by means of feeding a pressure controlled nitrogen stream (via PIC-131) to a throttle valve (V-175) which was open just enough to maintain a sufficient flow of this pressure controlled nitrogen stream through the throttle. The outlet of the product catch pot led into the pressurised line to the throttle valve. That way the nitrogen pressure determined the pressure in the product catch pot and reactor.

4.1.3 Guard catch pots

Two 1 liter stainless steel cylinders (each with a drain valve) were part of the experimental setup to act as guard catch pots in the gas supply lines (GCP-142 and -172). One of the guard catch pots was placed just before the reactor top gas inlet. The purpose of this guard catch pot was to protect the mass flow controller (FIC-122) from feed which would have been pumped right through to it in case of blockage downstream. The other guard catch pot was placed in the line via which the pressure regulator gas was fed to the throttle valve. The purpose of this guard catch pot was to protect the pressure indicator controllers (PIC-131 and -161, respectively) from the reactor product in case of a blockage in the throttle line. The two guard catch pots had a cone shaped bottom to ensure complete drainage when emptying. Lines leading to both catch pots from the gas

inlet side were fitted each with a check valve as an additional measure to prevent back flow and hence protect the preceding parts (FIC and PICs) from feed or product, respectively.

4.1.4 Introducing of feed

The feed was introduced into the reactor as a ready made mixture of the two reactants from a 2 liter glass container (FP-501) which was slightly heated at all times to 65°C by means of a hot plate. Heating was done in order to keep the feed mixture (which was partially solid at room temperature) in the liquid phase. An HPLC pump (PP-155, LabAlliance Series I) was used to pump the feed from the feed pot to the reactor inlet. The pump head and the line from the feed pot to the reactor inlet were also heated at all times to prevent feed from solidifying.

4.1.5 Reactor

The reactor (R-200) was made out of a stainless steel (SS 316) tube of length 453 mm and with an internal diameter of 19 mm (see figure 4-2). A 50 mm ¾ inch socket Swagelok VCR weld gland was connected to the top end of the reactor tube, also with an internal diameter of 19 mm, while the bottom end was closed by a cone shaped welded-in plate. This resulted in a reactor with a total length of 503 mm. A thermowell made of a 3.2 mm external diameter steel tube was fitted in the centre of the reactor tube, accessible from the bottom. The thermowell extended throughout the length of the reactor from about 20 mm from the top end of the reactor (point A in figure 4-2). A thermocouple was inserted into the thermowell. This thermocouple could be moved up and down and allowed the measurement of temperature at various points throughout the length of the reactor (TI-216 in figure 4-1). Another thermocouple (TI-211) was fitted to the top of the reactor extending to 1 cm from the top end of the central thermowell. This thermocouple was in a fixed position and was used to measure the temperature at the reactor inlet.

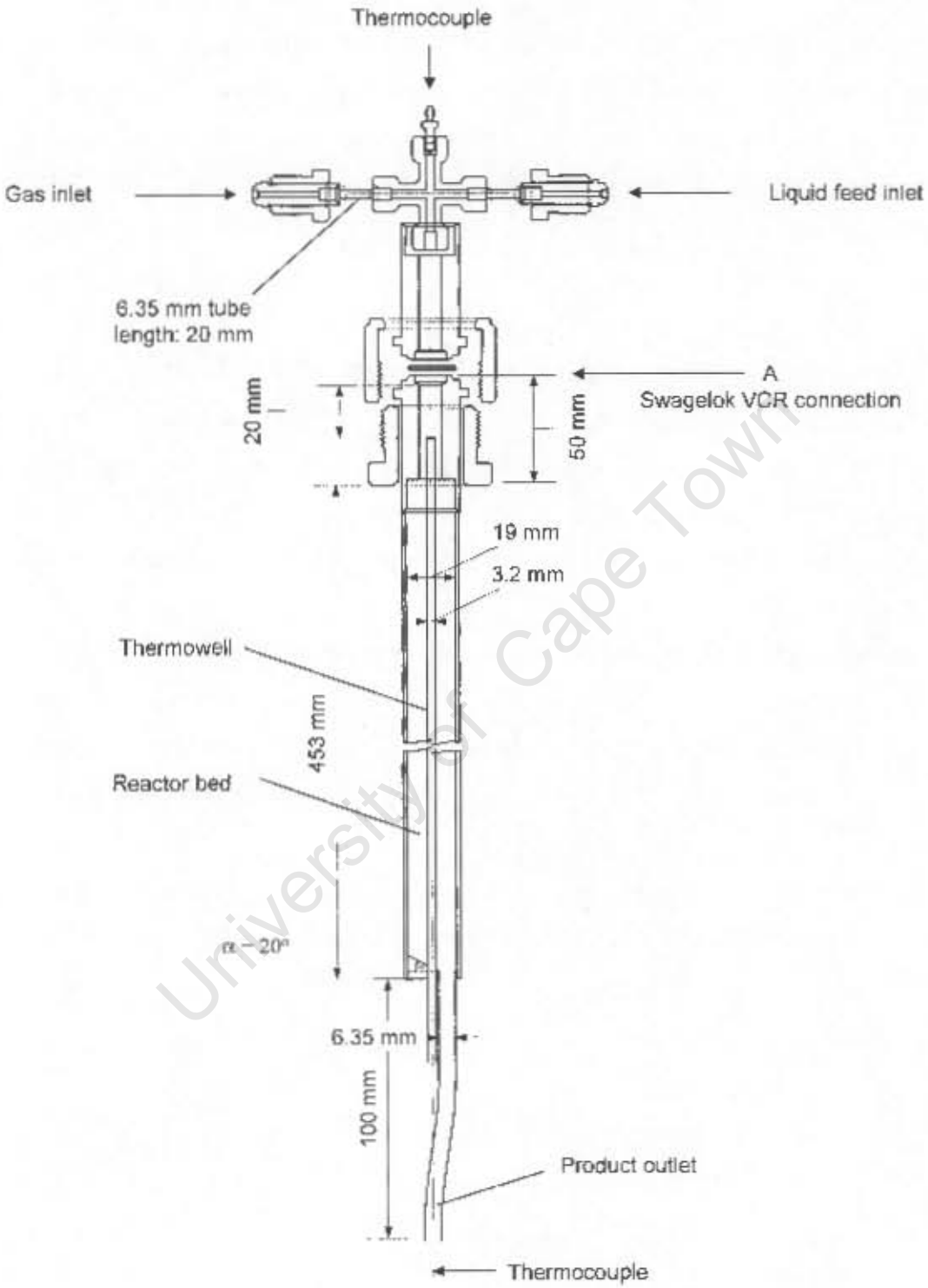


Figure 4-2: Detailed mechanical design of the reactor

There were four heating zones on the reactor (see figure 4-1). Each heating zone comprised of a cylindrical zinc sleeve and a cylindrical heating element. The zinc sleeves were put around the reactor tube next to each other. To each sleeve, a surrounding cylindrical heating element was connected and the heating elements were each connected to a temperature indicator controller (TIC-212 to TIC-215) as shown in figure 4-1. The heating elements on heating zone 1 to 4 were 6.3, 10, 12 and 10.3 cm long, respectively.

This arrangement served as a means to achieve an extended isothermal zone in approximately the middle the reactor for the catalyst bed (see figure 4-3). TIC-214, controlling the most central heating sleeve (heating zone 3, corresponding to the location of the reactor bed) was programmable. This was done in order to achieve a more controlled heating rate during catalyst activation.

The temperature profile in the reactor for operation at 300°C is shown in figure 4-3. It can be seen from the figure that the isothermal region in the reactor where the temperature was varying by ± 1°C was approximately 25 cm long ranging from around 15 to 40 cm from the top of the reactor (Point A in figure 4-2).

The catalyst bed was located approximately in the middle of this zone (see section 4.3.1 for details of catalyst loading and the total reactor packing).

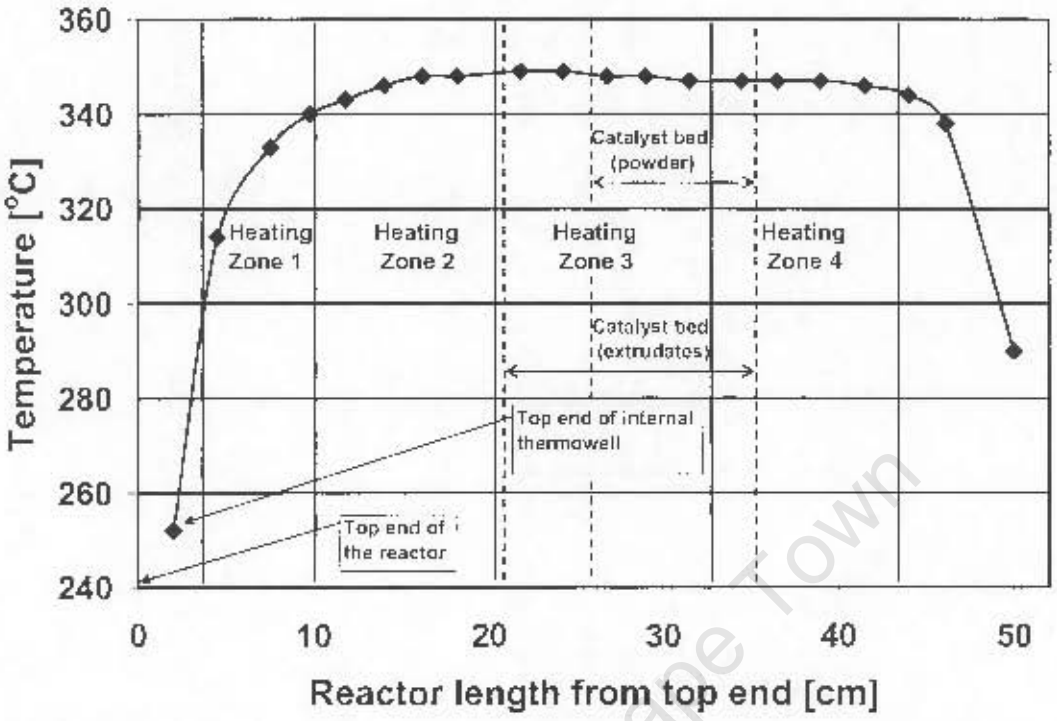


Figure 4-3: Temperature profile in the reactor bed. Length = 0 cm represents the top end of the reactor (point A in figure 4-2)

4.1.6 Product catch pot

A 500 cm^3 stainless steel cylinder was installed after the reactor in order to act as a product catch pot (see figure 4-4). The product catch pot was also cone shaped at the bottom to allow complete drainage. The connection at the top of the product catch pot that was coming from the reactor was extended right into the open volume of the pot and allowed the liquid component of the product from the reactor to collect in the catch pot and the traces of gaseous components to be vented off through the throttle valve. A drain valve for sampling was fitted to the bottom end of the product catch pot. The product catch pot was heated to 60°C (TIC-311) to prevent the liquid reactor product or part of it from solidifying. It was operated at reaction pressure, 60 bar, to keep low boiling products in liquid phase.

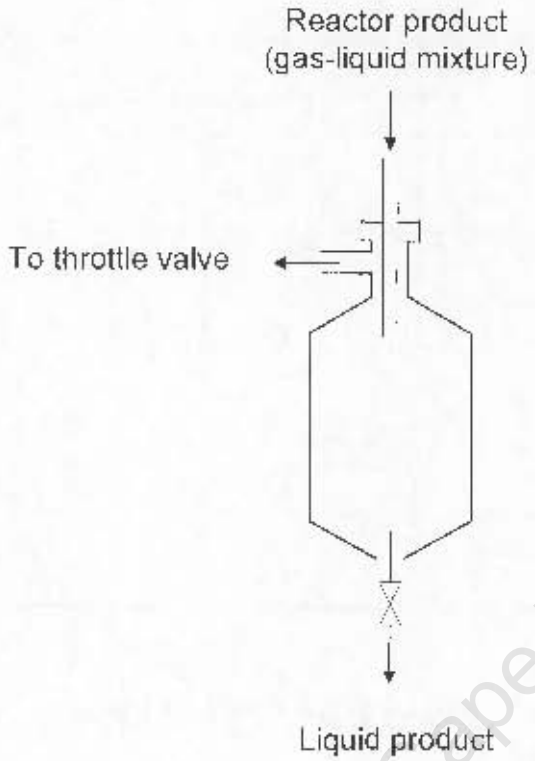


Figure 4-4: Cross-sectional view of the product catch pot

4.1.7 Emergency equipment

In case of pressure build up due to downstream blocking, a heated pressure relief valve (SV-154) on the line leading from the feed pump to the reactor inlet would have opened to release the pressure by discharging part of the contents of the apparatus into an emergency catch pot (CP-156). A second pressure relief valve (SV-162) was introduced to protect the low pressure controller (PIC-161).

4.2 Operating conditions

4.2.1 Searching for optimum reaction temperature and pressure

A 1:1 molar mixture of phenol and 2,5-xylenol was fed over a zeolite H-Beta catalyst with a SiO_2/Al_2O_3 molar ratio of 25 (table 4-1). This experiment was used for determining the operating temperature at which the different candidate catalysts were to be tested. Wide pore zeolite Beta was chosen because (i) medium pore zeolites such as ZSM-5 were expected not to catalyse transalkylation reactions of alkylaromatic compounds (due to spatial restrictions within the pore system – transition state shape selectivity) and (ii) because zeolite beta, despite being a wide pore zeolite, is known for its comparatively low coking tendencies.

Reactions were carried out in liquid phase. Based on experience from previous work done on phenol alkylation in the research group (Fletcher and Böhringer, 2004), a pressure of 60 bar was chosen to keep the feed mixture in liquid phase under reaction conditions (the boiling point of phenol at 60 bar is 419°C (Weast, 1980)).

Reactions were carried out over a temperature range of 250 to 450°C at a constant space velocity of 0.225 g_{feed} / $g_{catalyst}$ / hr. From results obtained (section 5.1) a temperature of 350 °C was chosen for catalyst screening experiments.

4.2.2 Catalysts screened

Table 4-1 lists the acid zeolite catalysts that were screened and their characteristic features. For details such as pore dimensions see section 2.12. These catalysts were all obtained from the supplier in their acidic form (H-form) and were used in this form.

Table 4-1: Zeolite catalysts that were screened and their characteristic features (supplier: Süd-Chemie)

Catalyst	*Molar SiO_2/Al_2O_3*	*Form*
H-ZSM-5 (H-MFI-90)	90	Crystal powder
H-Mordenite (H-MOR-90)	90	Extrudates (1/16") (ca. 20 wt% alumina binder)
H-Beta (H-BEA-25)	25	Crystal powder

4.2.3 Chemicals that were used

Table 4-2 lists the chemicals that were used for the reactions under study.

Table 4-2: Chemicals that were used

Compound	*Supplier*	*Purity (%)*
Phenol	Sigma-Aldrich	99
2,5-Xylenol	Sigma-Aldrich	97*
2,3,6-Trimethylphenol	Sigma-Aldrich	95*
Methanol	Sigma-Aldrich	99
Silicon carbide** (0.5 – 0.7 mm)	Colbern	-
Nitrogen	AirLiquide	99.99

*Major impurities were other xylenol and trimethylphenol isomers, respectively

**As catalyst diluent and for inert parts of the reactor packing, see figure 4-5

4.3 Experimental procedures

4.3.1 Catalyst loading

The catalyst was loaded as shown in figure 4-5. A layer of glass wool was placed at the bottom of the reactor to trap the packing. Inert material (silicon carbide) was packed up to 16.5 cm from the bottom of the reactor. This was to ensure that the catalyst bed was positioned within the isothermal zone which was starting at about 10 cm from the bottom of the reactor (see figures 4-2 and 4-3). 6 g of catalyst were mixed with 26 g of silicon carbide. Mixing the catalyst with silicon carbide was done to avoid pressure build up in the reactor bed when the catalyst was in the form of a crystal powder and to improve hydrodynamic flow patterns when the catalyst was in the form of extrudates.

The mixture of catalyst and silicon carbide was then loaded into the reactor on top of the bottom layer of silicon carbide. This occupied an additional length of ca. 10 cm (SiC / crystal powder mixture) or 15.5 cm (SiC / extrudates mixture), respectively. Silicon carbide was then packed on top of the catalyst bed up to the top of the reactor. The purpose of this top layer of silicon carbide was to preheat the feed and establish uniform flow of the feed mixture per cross-sectional area. Another layer of glass wool was put at the top of the reactor packing to prevent silicon carbide from being pushed back into the reactor inlet lines in case of an accidental backflow.

The tip of the thermocouple TI-216, which could be moved within the central thermowell (figures 4-1, 4-2 and 4-5) was adjusted in the middle of the catalyst bed.

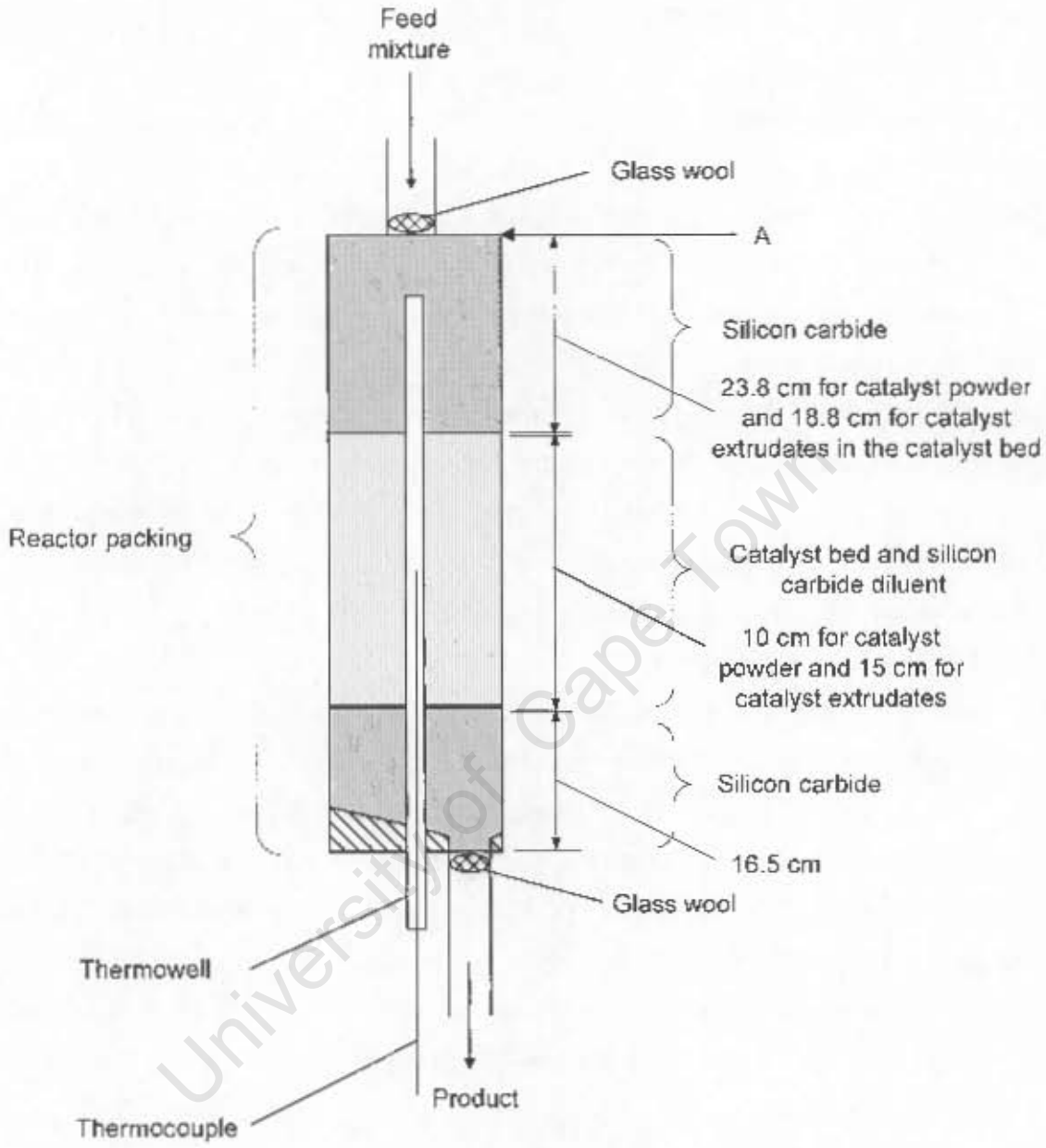


Figure 4-5: Cross-sectional view of the packed reactor

4.3.2 Catalyst drying and activation

Drying and activation of the catalyst was carried out in situ. Initially all valves were closed. A 500 sccm stream of nitrogen, supplied through the fully opened mass flow controller (FIC-122 in figure 4-1), was passed through the reactor at atmospheric pressure with valves V-112, V-145, V-175 and V-176 then open. The temperature in the catalyst bed was increased from room temperature to the initial reaction temperature, e.g. 350°C, at a rate of 1°C per minute, with periods of 1 hour each when the temperature was kept constant at 90, 100 and 110°C. This was in order to remove adsorbed moisture very cautiously. When the reaction temperature was reached, the nitrogen flow was stopped (V-112 and V-145 closed and FIC-122 switched off) and the exit valves V-175 and V-176 were closed to isolate the catalyst bed from the atmosphere. The temperature was kept at reaction temperature until the reaction was started.

4.3.3 Start up

Initially all valves were closed. The nitrogen supply line was opened by opening valve V-112 and a pressure of about 65 bar was set on PIC-113. Valves V-121 (MFC by-pass) and V-145 were opened to allow gas flow into the reactor. When a pressure of 60 bar was reached in the reactor (indicated by PI-144 and PI-174), valves V-121 and V-145 were closed. A pressure of 60 bar was set on PIC-131 for pressure control purposes. The three way valve V-132 was then turned in the direction of PIC-131 to allow nitrogen flow through check valve CV-171 and into the rest of the system. This was meant to control the pressure in the system. Valve V-176 was opened. The line leading from valve V-176 to the exhaust was connected to a bubble meter. The throttle valve V-175 was slowly opened slightly until a gas flow of between 20 and 30 ml/min was measured on the bubble meter. The pressure on PIC-131 was then accurately adjusted to make sure that the reading on PI-174 was exactly 60 bar.

Valve V-153 was opened for priming the feed inlet line. A transparent plastic hose tube was connected to the end of the steel line leading from valve V-153. The feed pump PP-155 was switched on and was set to prime mode. Feed coming out of the hose tube was collected in a glass beaker. Priming was done until no bubbles were visible in the transparent hose tube. This was to ensure that there were no leaks in the line from the feed pot to the pump and in the pump head itself. Then priming was stopped and valve V-153 was closed.

Valve V-152 was opened. Priming was continued until the temperature at the reactor inlet, indicated by TI-211, fell by ca. 10°C. Then the pump was stopped again. Priming of the reactor top was done to make sure that the hold up volume of the test unit upstream the reactor was filled, hence ensure a steady flow of feed from the start of the operation. The pump was set at the initial flow rate for the experiments, e.g. 0.01 ml/min and was started simultaneously with a stopwatch used to determine time-on-stream. Valve V-312 on the product catch pot, CP-300, was opened for a short period of time to ensure that the pot was empty at the beginning.

4.3.4 On-stream operation

During operation, samples were taken (once a day for a pump rate of 0.01 ml/min and more often, correspondingly, for higher pump rates) by completely emptying the contents of the product catch pot CP-300 through valve V-312 into screw lid glass bottles of between 50 and 150 ml. Empty and full bottles were weighed in order to check for proper pump operation. The samples were analysed immediately to check for steady state of the reaction. When steady state was reached, conditions were changed according to the experimental program. For each sample, time on the stopwatch, pressure on PI-174 and the temperature indicated on TI-216 were recorded and pressure and temperature, if necessary, were readjusted.

4.3.5 Shut down

After collection of the last sample, the reaction was stopped by first switching off the pump and then closing valve V-132 to stop the pressure control gas supply. The system was then allowed to depressurize to ambient pressure through the opened throttle valve V-175. Nitrogen was introduced from top (via opening valves V-145 and, slightly, V-121) to flush the reactor and remove all reactor contents that were volatile at the reaction temperature. After ca. 1 hour, the temperature controllers for the reactor heating sleeves were set to zero to allow the reactor to cool down to room temperature. Then the nitrogen flow was stopped.

4.4 Production of simulated technical mixture

No tetra- or penta-methyl phenols were commercially available. In order to study the transalkylation of such compounds with phenol and simulate a possible technical feed stream, such a feed had to be made in-house. For this purpose, methanol was reacted with both 2,5-xylenol and 2,3,6-trimethylphenol, in a 10 : 1 molar ratio each, to produce a mixture that simulates an industrial feed (technical mixture). These reactions were carried out over 20 g H-BEA-25 catalyst mixed with 60 g silicon carbide at 400°C, 60 bar and a space velocity (WHSV) of the mixture methanol and 2,5-xylenol or 2,3,6-trimethylphenol of 0.2 h^{-1}. A second, similar test unit as in the case of the phenol and 2,5-xylenol reactions was used and similar operation procedures were applied.

The full length of the reactor in this unit was packed with the aforementioned mixture of catalyst and silicon carbide. This was because accurate isothermal operation was not relevant in this case. The only objective was to produce a range of methylphenols consisting mainly of the higher ones (C_{9+}).

1300 cm^3 of raw organic product mixture was collected. The mixture was distilled under vacuum in order to minimise the amount of low methylphenols (C_{8-}) and other low boiling compounds that may have formed from the methanol. A Büchi rotavapour with a thermostated oil bath (type B-400), a vacuum controller (type V-800) and a rotavapour (type B-205) was used. The bath was set at its maximum temperature of 180°C and the pressure was reduced from 1 bar to 250 mbar in steps of 50 mbar at 1 hour intervals. About 500 ml of high boiling residue was obtained from the distillation.

After analysis, see table 5-2, this residue was mixed with phenol to produce an approximately 20 : 1 molar ratio of phenol : residue. This mixture was then fed to the reactor in the regular test unit at 350°C and 60 bar over 6 g of the H-BEA-25 catalyst at changing space velocities.

4.5 2,5-xylenol isomerisation

To determine the distribution of the xylenol isomers without being affected by the parallel transalkylation reaction with phenol, 2,5-xylenol was isomerised at 350°C and 60 bar over 6 g of H-BEA-25 catalyst. The feed was highly diluted with benzene to suppress disproportionation reactions. Benzene acted as an inert solvent at the reaction conditions applied. The same test unit as mentioned in section 4.4 and a similar operation procedure was applied. The reaction was carried out at two different space velocities (WHSV) of 0.225 h^{-1} and 0.90 h^{-1}.

4.6 Product analysis

Product analysis was done by gas chromatography. A gas chromatograph (GC) with a Flame Ionisation Detector (FID) was used. The specifications of the GC and GC column used are listed in table 4-3.

Table 4-3: Specifications of the GC and GC column used for product analysis

GC	Varian 3900
Autosampler	Varian CP-8400
Column manufacturer	Supelco
Type of column	Fused silica capillary, wall coated
Column length	30 m
Column internal diameter	0.25 mm
Stationery phase	Alpha Dex 120 (containing 5 % crown ethers)
Film thickness	0.25 μm
Carrier gas	Hydrogen
Split ratio	30
Volume injected	10 μl of diluted sample (see below)
Injector temperature	280 °C
Column flow	1 ml/min (constant)
Detector	FID
Temperature programme	Isothermal at 100 °C for 6 minutes Ramped at 8 °C / min to 220 °C Isothermal at 220 °C for 20 minutes

From sample bottles, about 0.5 ml of product was transferred into 2 ml autosampler bottles for GC analysis. This was then diluted with acetone, ca. 3 : 1 by volume. A typical chromatogram obtained from the GC analysis of the transalkylation products from reacting phenol with 2,5-xylenol is shown in figure 4-6. Chromatograms obtained from the simulated technical mixture together with

co-reactant phenol and from reacting phenol with the simulated technical mixture and 2,3,6-trimethylphenol are shown in appendix E. The chromatogram obtained from the simulated technical mixture and added phenol, before reaction, is also shown in appendix E.

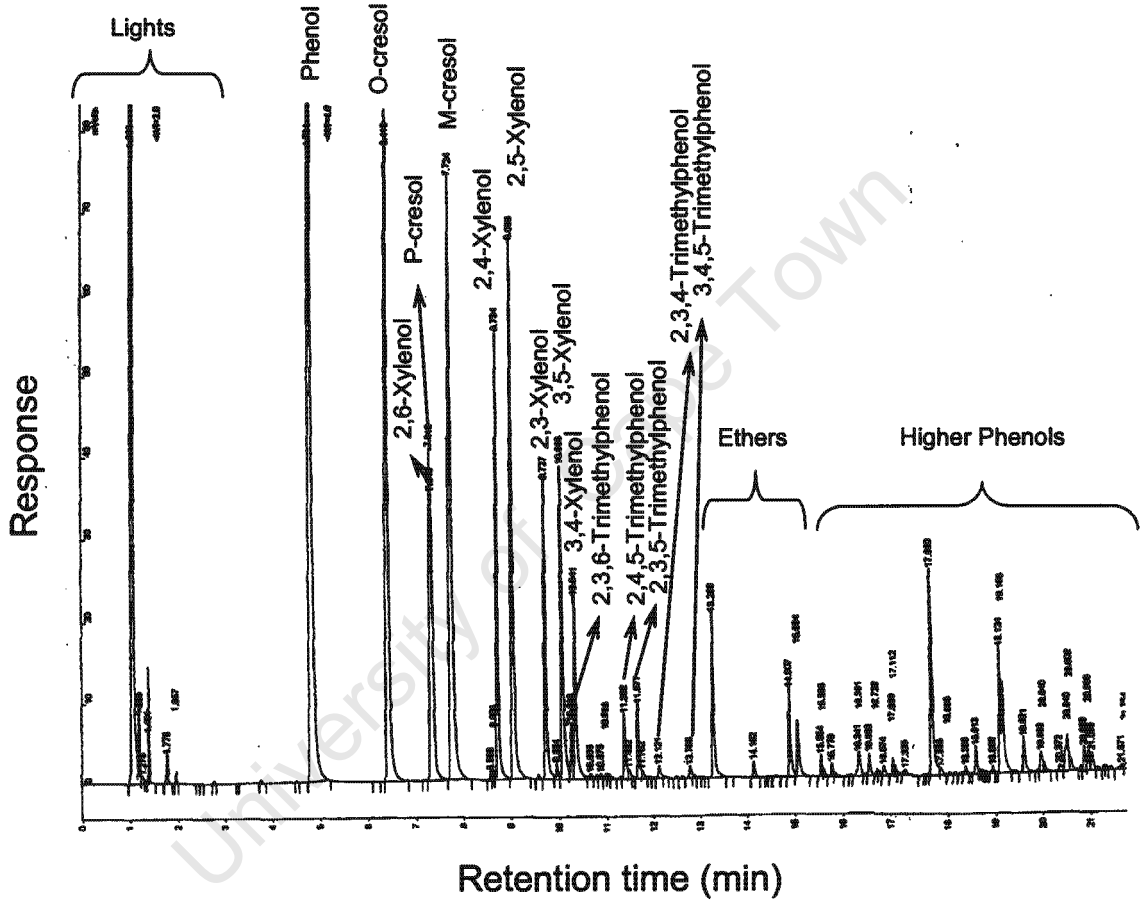


Figure 4-6: Typical chromatogram as obtained from the GC analysis of the product of phenol transalkylation with 2,5-xylenol

To identify the peaks on the chromatogram of the product samples, reference mixtures containing different amounts of the compounds that were expected to be present in the product samples were prepared. Samples of the product mixtures, spiked with small amounts of these reference mixtures, were injected. This enhanced the peak areas of the compounds which were present in both the

product mixture and in the reference mixtures. This way the different peaks of the different compounds were identified. A GC-MS (gas chromatograph mass spectrometer combination) was used for further identification of peaks in particular of higher compounds of which samples were not commercially available.

4.7 Data work up

The amounts of the different compounds present in a sample are represented by the peak areas generated by the GC's Flame Ionization Detector (FID) signal integrator. The FID responds to the ionization of carbon atoms and hence, the concentration of carbon in the effluent of the GC column determines the intensity of the FID signal. However, the contribution of each carbon atom to the intensity of the FID signal depends also on the nature of other atoms bonded to it. The FID response of a carbon atom that is only surrounded by carbon – carbon or carbon – hydrogen bonds is 1, while in case of a carbon – oxygen bond, as in phenols, it is 0.55 (Callanan, 1999) and in case of a carbon atom bonded to an oxygen atom with a double bond it is 0. As a result peak areas were converted to mol proportional values considering the presence of oxygen atoms in the molecules (section 4.7.1).

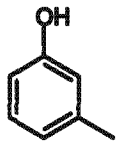
4.7.1 Calculation of mol proportional values from peak areas

Mol proportional values, MPV's, were calculated by dividing the peak area by the sum of the responses of the individual carbon atoms in the compound as shown in equation 4-1.

$$response = N_{C,\,full\ response,\,i} + N_{C,\,partial\ response,\,i} \times 0.55 \qquad \text{Equation 4-1}$$

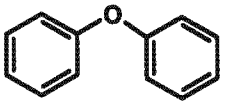
(with N_C = number of carbon atoms)

Examples of how MPV's were calculated from peak areas A_i for a cresol and for diphenylether are shown in equations 4-2 and 4-3.



m-cresol

$$MPV_{m-cresol} = \frac{A_{m-cresol}}{6\times1+1\times0.55} \qquad \text{Equation 4-2}$$



diphenylether

$$MPV_{diphenylehter} = \frac{A_{diphenylether}}{10\times1+2\times0.55} \qquad \text{Equation 4-3}$$

Normalising all the MPV's results in molar fractions f_i of every compound i in the product mixture.

4.7.2 Calculation of conversion, yield and selectivity

In order to compare different catalysts, and under changing reaction conditions, conversions, yields and selectivities were calculated as shown in equations 4-4 to 4-7. These calculations were done on the basis of a phenol ring or mol balance with the assumption and proof supported by the mass balance of pumped feed and weighed product, that the number of phenol rings that entered the reactor was equal to the number of phenol rings that exited the reactor.

Conversions were calculated as follows:

$$X_{phenol} = \frac{f_{phenol,feed} - f_{phenol,product}}{f_{phenol,feed}} \qquad \text{Equation 4-4}$$

$$X_{2,5-xylenol} = \frac{f_{2,5-xylenol,feed} - f_{2,5-xylenol,product}}{f_{2,5-xylenol,feed}}$$ Equation 4-5

Yields are equal to the molar percentage of each component in the reactor product, according to equation 4-6.

$$Y_i = f_i$$ Equation 4-6

Selectivities were calculated from yields based on the total conversion of phenol plus 2,5-xylenol as given in equation 4-7.

$$S = \frac{Y_i}{X_{total}}$$ Equation 4-7

The total conversion X_{total} is the weighed average of the individual conversions of phenol and 2,5-xylenol according to the composition of the feed.

Calculations were analogous for 2,3,6-trimethylphenol co-feed and the simulated technical co-feed (see section 4.4).

Chapter 5

RESULTS

In this chapter, the experimental results are presented that were obtained in the transalkylation reaction between phenol and 2,5-xylenol over zeolites H-MFI-90, H-MOR-90 and H-BEA-25 and phenol and 2,3,6-trimethylphenol as well as phenol and the simulated technical mixture (see section 4.4) over zeolite H-BEA-25 (see appendix F). Experiments that were carried out are listed in table 5-1.

Table 5-1: List of experiments that were carried out (in liquid phase at 60 bar, throughout) with mixtures of phenol and different co-feeds

Exp	*Catalyst*	*Temperature (°C)*	*$WHSV_{total}$ (h^{-1})*	*Co-feed**	*Molar ratio***	*TOS*** (hrs)*
1	H-BEA-25	250 - 350	0.45	Xyl	1 : 1	319
2	H-BEA-25	400 - 450	0.45	Xyl	1 : 1	347
3	H-BEA-25	350	0.113 – 0.45	Xyl	1 : 1	299
4	H-MOR-90	350	0.113 – 0.45	Xyl	1 : 1	191
5	H-MFI-90	350	0.113 – 0.45	Xyl	1 : 1	249
6	H-MOR-90	350	0.113 – 0.45	Tmp	1 : 1	349
7	H-BEA-25	350	0.113 – 0.45	Xyl	5 : 1	566
8	H-BEA-25	350	0.113 – 0.45	Xyl	20 : 1	372
9	H-BEA-25	350	0.113 – 0.45	Tech	20 : 1	359
10	H-BEA-25	350	0.113	Xyl	1 : 1	226
11	H-BEA-25	350	0.225 – 0.90	****	-	112

*Xyl = 2,5-xylenol, Tmp = 2,3,6-trimethylphenol, Tech = simulated technical mixture

**Phenol : co-feed, molar ratio

***Time-on-stream

**** Feed was 2,5-xylenol in inert benzene solvent (in approximately 5 : 1 volume feed : solvent ratio)

Results are presented in their primary form as conversions, yields and selectivities versus time-on-stream and versus the conversion of the higher methylated feed compound (2,5-xylenol or 2,3,6-trimethylphenol respectively).

From the different experiments, average conversion, average selectivity and average yield were determined by taking an average of the data points generated with a catalyst under the same conditions after the experimental condition has settled in, i.e., a kind of steady state was reached. These averages of data are presented versus the varied reaction conditions.

5.1 Operating temperature for comparing catalysts

To identify an optimum operating temperature for comparing the different catalysts, two temperature series were carried out with a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol over H-BEA-25 catalyst at a space velocity of 0.45 h^{-1} ranging from 250 – 350°C and 400 – 450°C, respectively. The results shown in figures 5-1 to 5-5 were obtained.

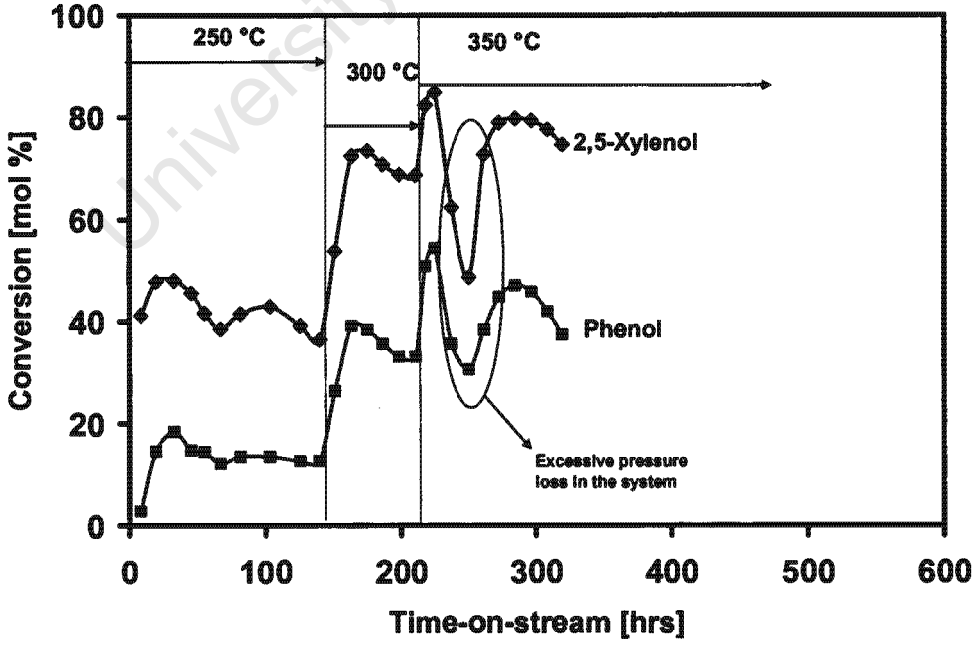


Figure 5-1 (Experiment 1): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.45 h^{-1}

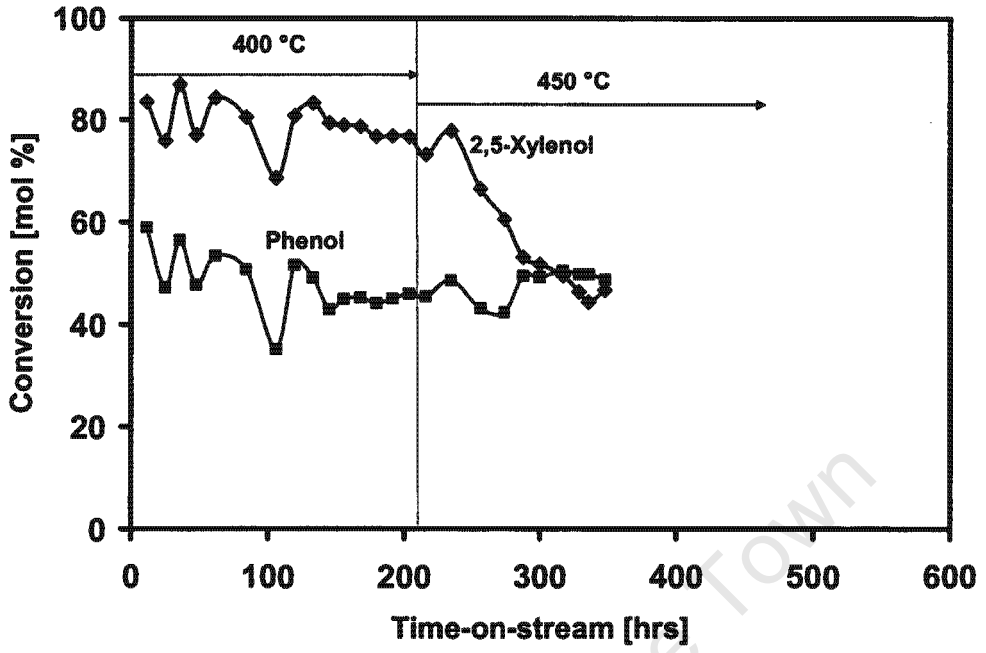


Figure 5-2 (Experiment 2): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.45 h^{-1}

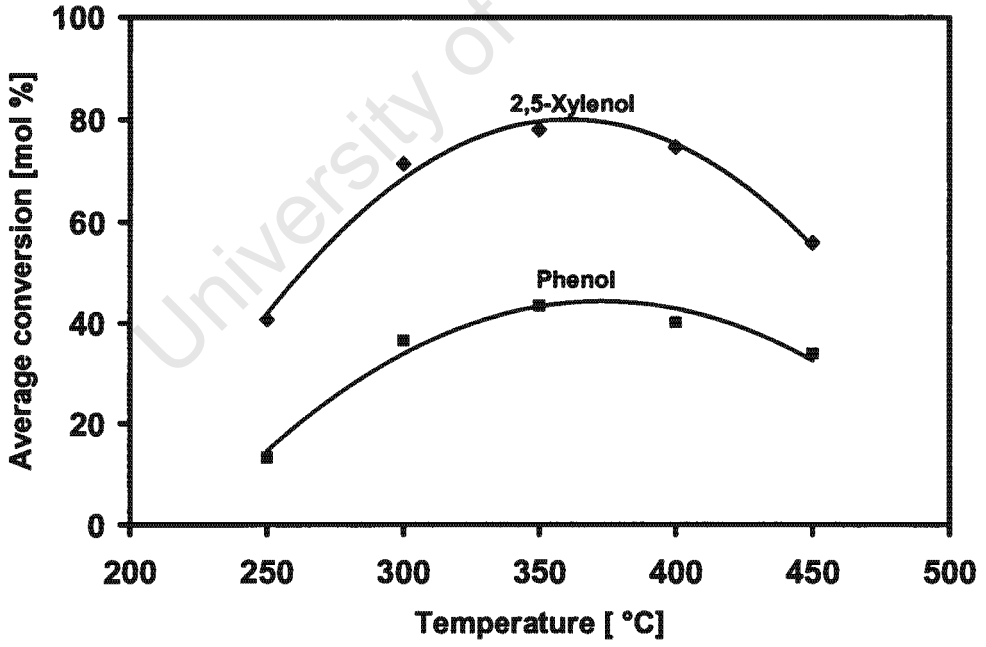


Figure 5-3 (Experiments 1 and 2): Average conversion versus temperature over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.45 h^{-1}

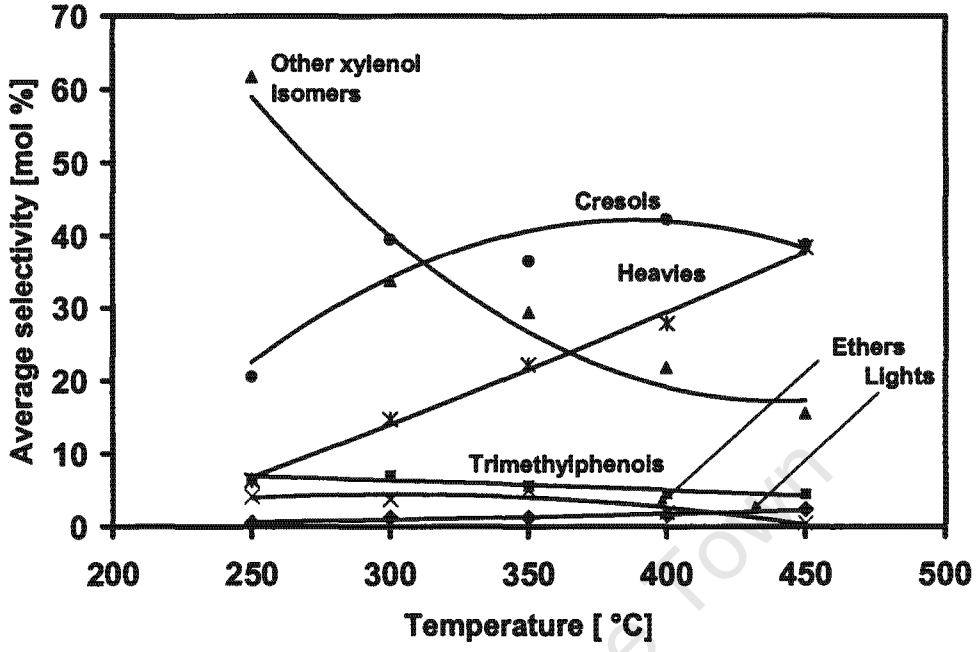


Figure 5-4 (Experiments 1 and 2): Selectivity versus temperature over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.45 h^{-1}

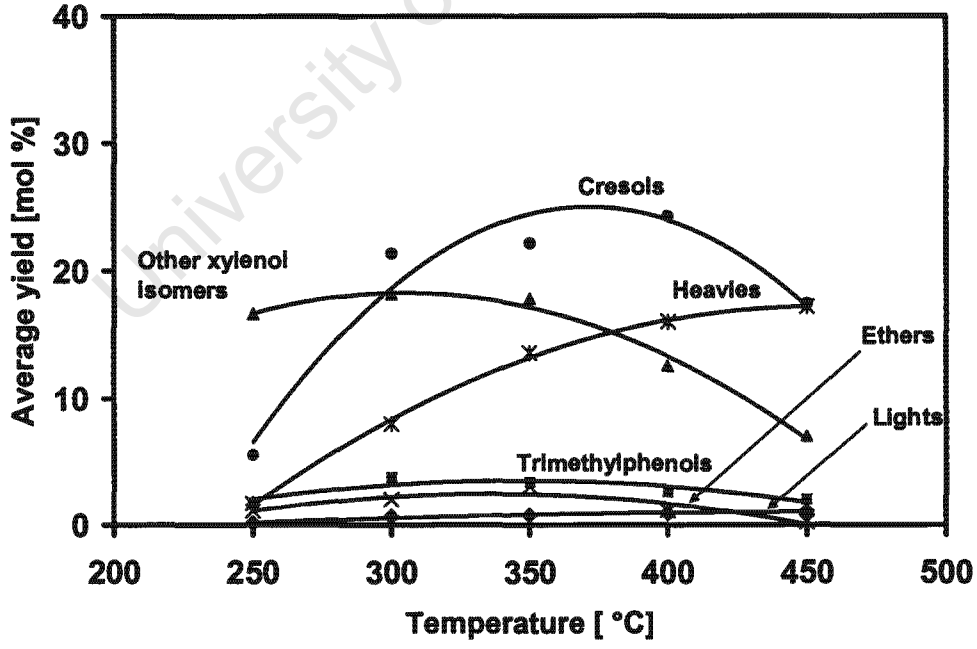


Figure 5-5 (Experiments 1 and 2): Yield versus temperature over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.45 h^{-1}

Figure 5-1 shows that the conversion of both feed components, phenol and 2,5-xylenol, increases with increasing temperature from around 40 mol % for 2,5-xylenol and around 17 mol % for phenol at 250°C to around 80 mol % and slightly above 40 mol %, respectively, at a temperature of 350°C. The reaction at 400 and 450°C (figure 5-2) had to be done with a fresh load of catalyst due to a blockage occurring in the test unit while running at a temperature of 350°C. After initially going through significant fluctuations of the data at 400°C due to abnormal pressure variations in the system, the conversion settled at around 75 mol % for 2,5-xylenol and less than 50 mol % for phenol (figure 5-2). At 450°C, the conversion of 2,5-xylenol declines rather steeply by around 40 mol % points during ca. 100 hours on stream, after which the reaction was stopped. The conversion of phenol remains constant at almost the same level as at 400°C (figure 5-2). Note that the reaction system may not have been in liquid phase anymore at 450°C. Unfortunately, no repeat of a lower temperature setting was carried out after running at 450°C.

Figure 5-3 shows that the average conversions increase simultaneously with increasing temperature from around 40 mol % for 2,5-xylenol and 15 mol % for phenol at 250°C, and reach maxima at 80 mol % and 40 mol %, respectively, at around 350°C. With temperature increasing further, the average conversions start declining to around 55 mol % for 2,5-xylenol and 35 mol % for phenol at the final experimental temperature of 450°C.

Figure 5-4 shows that the average selectivity for the cresols, the desired transalkylation products, increases with increasing temperature from around 22 mol % at 250°C and reaches a maximum at around 42 mol % between 350°C and 400°C. Beyond 400°C, the selectivity for cresols starts declining to around 40 mol % at 450°C. The average selectivity for other xylenol isomers (i.e. other than the feed component 2,5-xylenol) is high at low temperature and decreases steeply with increasing temperature from 60 mol % at 250°C to around 17 mol % at 450°C. The average selectivity for the heavies increases steeply and more or

less constantly with increasing temperature from around 7 mol % at 250°C to around 40 mol % at 450°C. The average selectivities for trimethylphenols and ethers show a slight decrease with increasing temperature from about 7 mol % and 4 mol %, respectively, at 250°C to about 5 mol % and 0 mol %, respectively, at 450°C. The average selectivity for lights is low but shows an increase from about 1 mol % at 250°C to about 3 mol % at 450°C.

Figure 5-5 shows yields. The average yield of cresols increases with increasing temperature from 250°C and reaches a maximum of about 25 mol % between 350°C and 400°C but declines to about 18 mol % at 450°C. The average yield of other xylenol isomers is almost uninfluenced by increasing temperature at about 19 mol % between 250°C and 300°C and then declines to about 7 mol % at 450°C. The average yield of heavies increases steeply with increasing temperature from about 2 mol % at 250°C to a maximum of about 17 mol % at 450°C. The average yield of trimethylphenols and ethers is very low but increases slightly with increasing temperature from about 3 mol % and 2 mol %, respectively, at 250°C to a maximum of about 4 mol % and 3 mol %, respectively, at a temperature of 350°C and then declines to about 3 mol % and 0 mol %, respectively, at 450°C. The average yield of lights increases with increasing temperature from about 0 mol % at 250°C to about 2 mol % at 450°C.

From these results a temperature of 350°C was chosen for further experimentation.

5.2 Catalyst deactivation

To study catalyst deactivation or stability, respectively, experiments were run under constant conditions for more than 200 hours on stream with a feed mixture of 1 : 1 molar ratio of phenol and 2,5-xylenol over H-BEA-25 catalyst at a temperature of 350°C with a space velocity of 0.113 h^{-1} in one case and 0.45 h^{-1} in another case. The results obtained are presented as plots of conversion versus time-on-stream in figures 5-6 and 5-7.

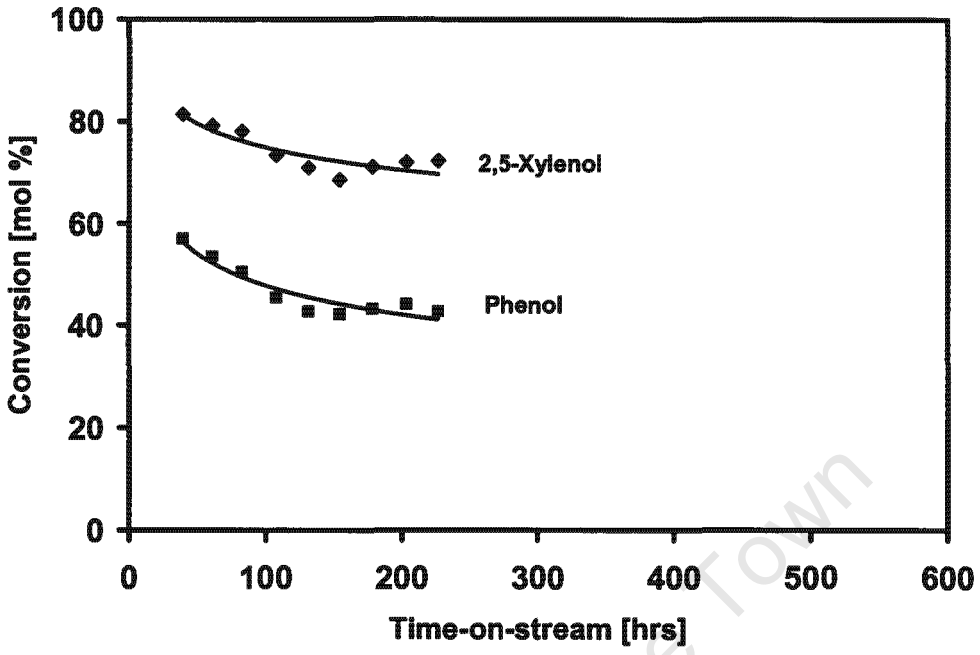


Figure 5-6 (Experiment 10): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

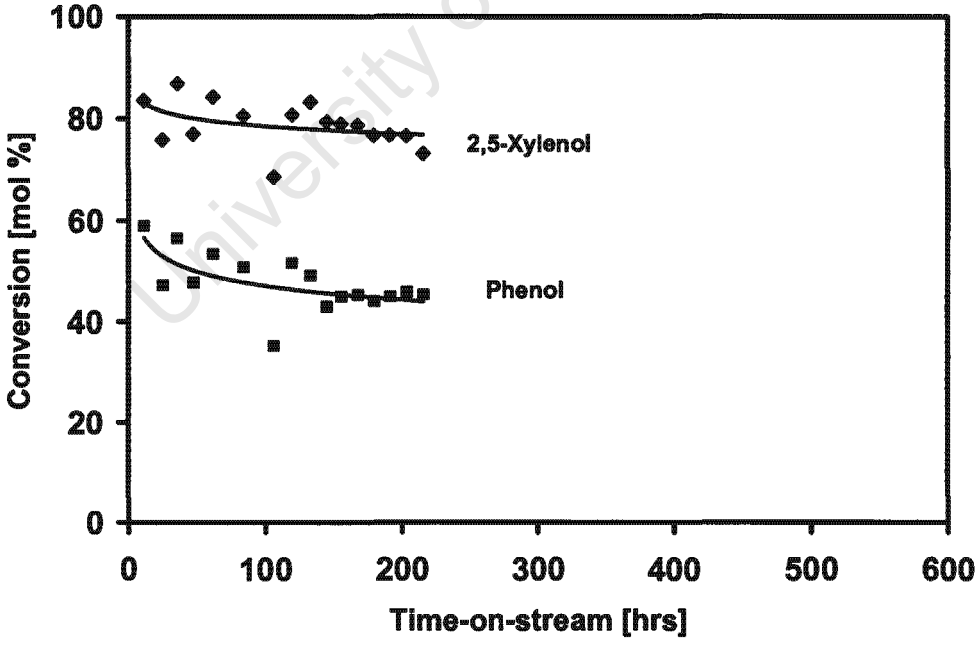


Figure 5-7 (Experiment 2): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 400°C and a space velocity (WHSV) of 0.45 h^{-1}

The other stability experiments were carried out by comparing conversion when an earlier condition was repeated within the same run, i.e., with the same charge of catalyst, just longer used. This was done with H-BEA-25 catalyst at a temperature of 350°C for reaction mixtures with molar feed ratios of 1 : 1 and 5 : 1 of phenol and 2,5-xylenol at a space velocity of 0.113 h^{-1}. The results obtained are shown in figures 5-8 and 5-9.

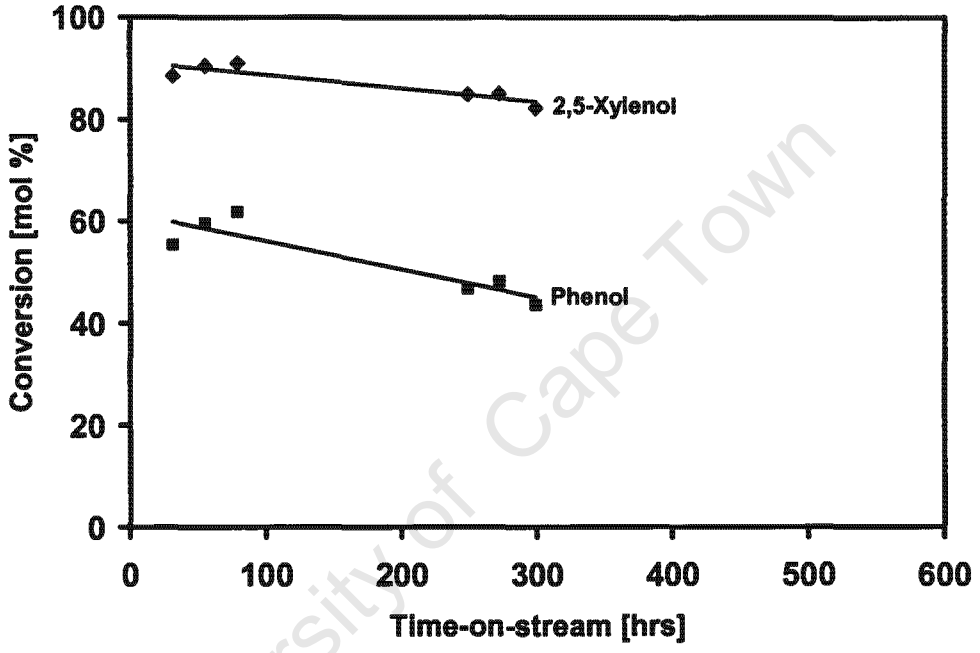


Figure 5-8 (Experiment 3): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

5.3 Repeatability

Results of the runs described in section 5.2 also confirm sufficient repeatability of experiments.

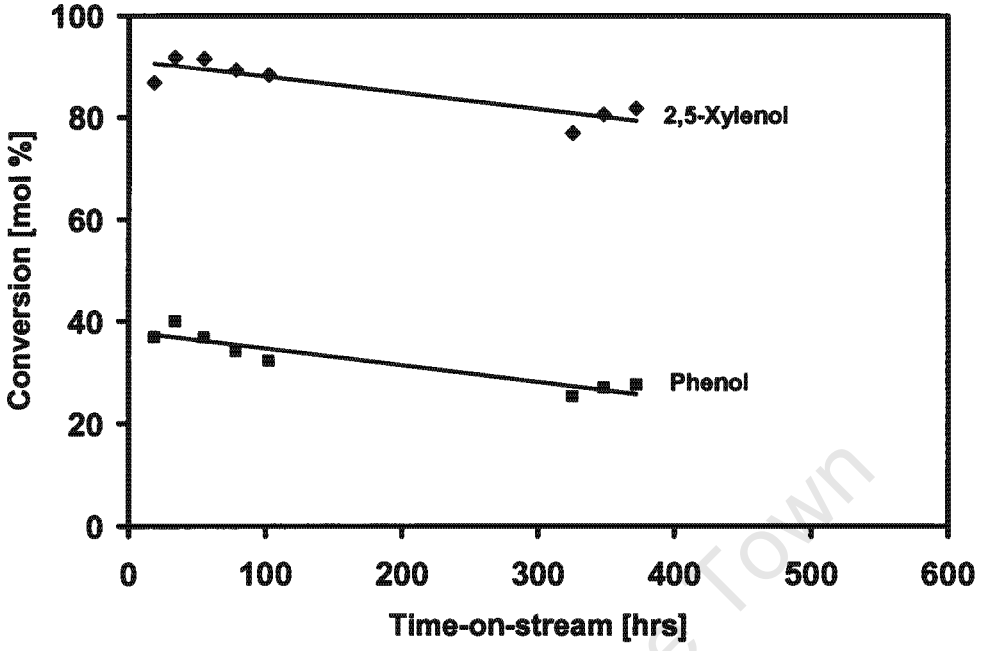


Figure 5-9 (Experiment 7): Conversion versus time-on-stream over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

Figures 5-8 and 5-9 show that the conversions at the repeated condition are just slightly lower than the conversions at the end of the initial settling-in period.

5.3.1 Repeatability of results within an individual run

Two experiments were carried out over H-BEA-25 zeolite with the initially applied conditions of 350°C, space velocity (WHSV) of 0.113 h^{-1} and the molar ratios of 1 : 1 and 5 : 1, respectively, of phenol and 2,5-xylenol in the feed mixture repeated after extended time-on-stream with other condition settings applied in between.

The obtained conversions have already been shown in figures 5-8 and 5-9. Figures 5-6 and 5-7 show, by the initially fast declining conversion, that the catalyst deactivates rather fast during the first 100 hours on stream after which the catalyst exhibits better stability, working in a quasi steady state of activity for

the rest of the experiment lasting over more than a hundred hours additionally. Almost the same conversions were achieved in the repeated setting as in the initial settling in period, the difference essentially reflecting the comparably rapid decline of activity at the beginning of the runs.

Selectivities repeatability within the runs appears a little worse (see figures 5-10 and 5-11), however, this is mainly due to the initially rather high selectivities to heavies and lights over the fresh catalyst, which are rapidly declining within a short period of time-on-stream (see e.g. figure 5-14).

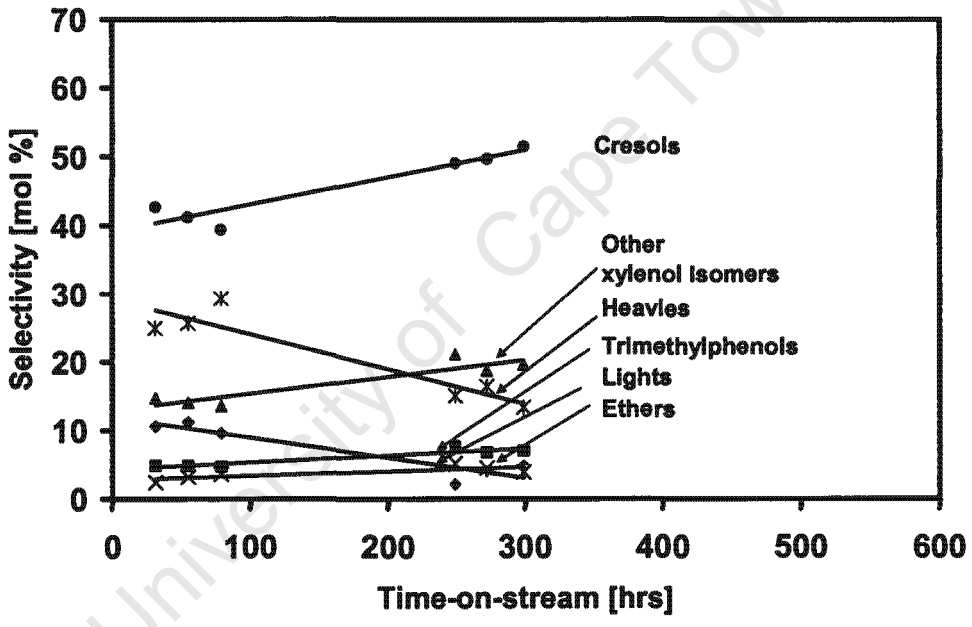


Figure 5-10 (Experiment 3): Selectivity versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

5.3.2 Repeatability of runs

Two runs under identical reaction conditions over catalyst H-BEA-25, 350°C, space velocity (WHSV) of 0.113 h^{-1}, molar ratio of phenol and 2,5-xylenol in the feed mixture of 1 : 1, show the repeatability of runs.

Figures 5-6 and 5-8 showed conversions in these runs versus time-on-stream individually. Data points are combined in a single graph in figure 5-12.

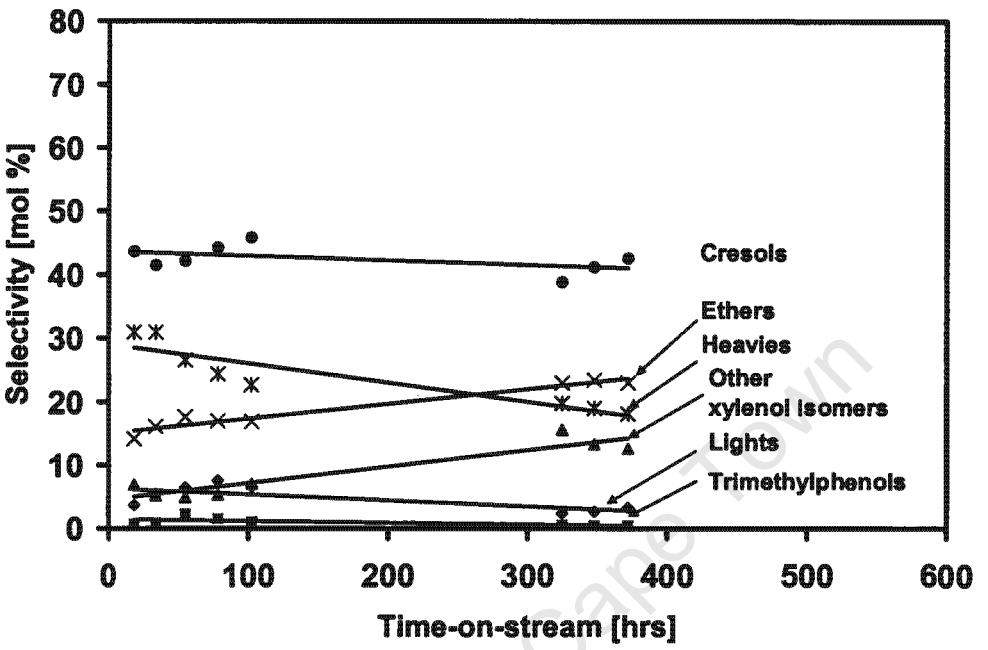
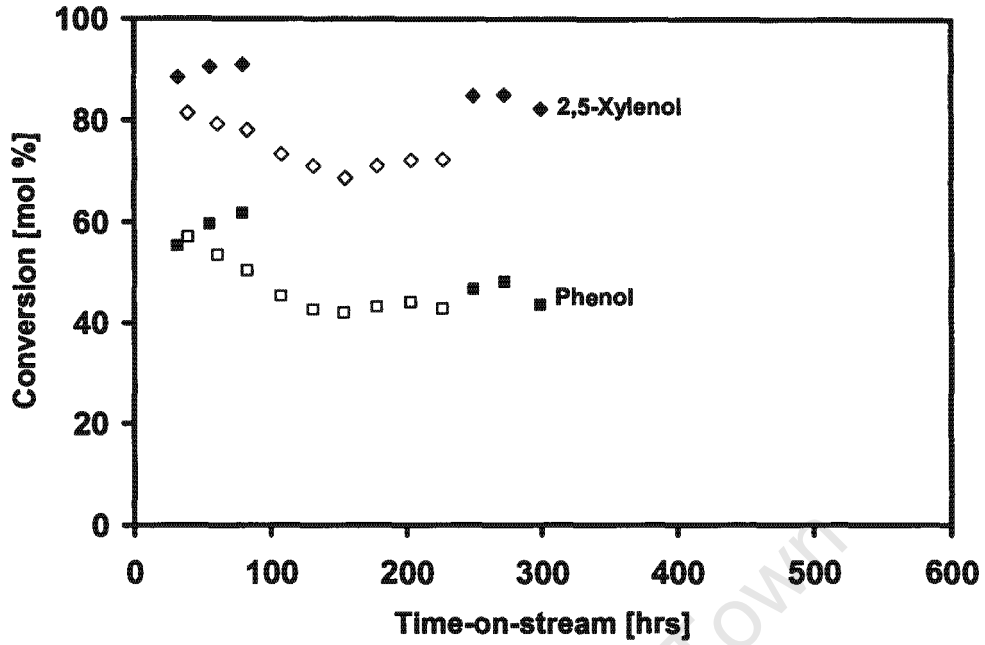


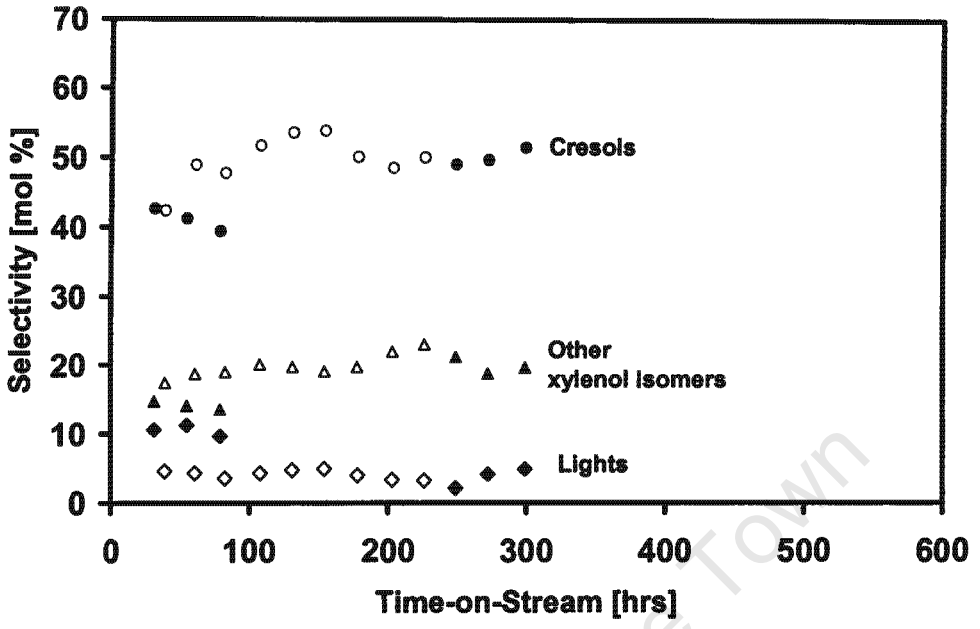
Figure 5-11 (Experiment 7): Selectivity versus time-on-stream over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}



Full symbols: First run (experiment 3)
Open symbols: Repeat run (experiment 10)

Figure 5-12 (Experiments 3 and 10): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

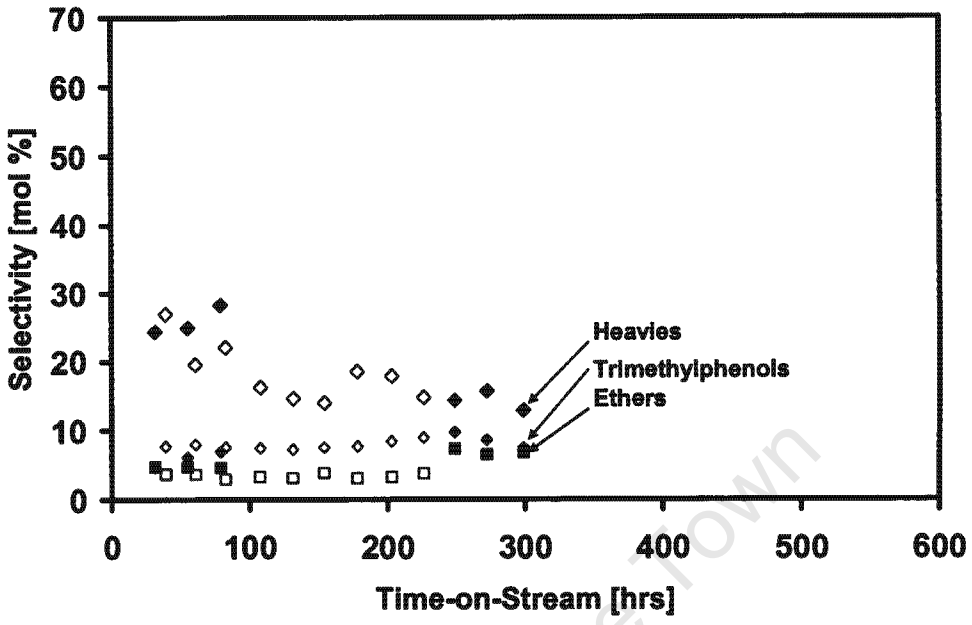
Selectivities obtained from one of the runs have already been shown in figure 5-10. Data points of the other run are added and the combined data are shown in figures 5-13 and 5-14.



Full symbols: First run (experiment 3)
Open symbols: Repeat run (experiment 10)

Figure 5-13 (Experiments 3 and 10): Selectivity versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

It follows from figures 5-12 to 5-14 that, except some deviations during the initial setting in periods, repeatability of runs is good.



Full symbols: First run (experiment 3)
Open symbols: Repeat run (experiment 10)

Figure 5-14 (Experiments 3 and 10): Selectivity versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and a space velocity (WHSV) of 0.113 h^{-1}

5.3.3 Comparability of results

Repeatability studies show that repeating reaction conditions during a run and repeating runs leads to very similar results, with the effect of catalyst deactivation with time-on-stream being negligible, provided initial data points (up to ca. 100 hours on stream) are ignored. Repeatability studies indicate also, that results from runs with different catalysts can be compared.

5.4 Comparing catalysts

Catalyst screening experiments were carried out over catalysts H-MFI-90, H-MOR-90 and H-BEA-25 (table 4-1) at a temperature of 350°C with a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol over a range of space velocities. The three catalysts were compared in terms of conversion, selectivity and yield. The results obtained are presented in figures 5-15 to 5-23.

Figures 5-15 to 5-17 show phenol and 2,5-xylenol conversions versus time-on-stream. Data indicates that conversion decreases with increasing space velocity for all the three catalysts tested. Higher conversion at all space velocities are obtained on both zeolites H-MFI-90 and H-BEA-25 than on zeolite H-MOR-90. At a weight hourly space velocity (WHSV) of 0.113 h^{-1}, 2,5-xylenol conversions of about 90 mol % are obtained on the former two zeolites, as well as similar phenol conversions of around 64 mol % and around 60 mol %, respectively.

However, both phenol and 2,5-xylenol conversions at the higher space velocities of 0.225 and 0.45 h^{-1} are higher for H-BEA-25 than for H-MFI-90, with around 85 mol % 2,5-xylenol and around 50 mol % phenol conversion on H-BEA-25 compared to around 75 mol % 2,5-xylenol and around 33 mol % phenol conversion on H-MFI-90 at a space velocity of 0.225 h^{-1}. After doubing the space velocity a second time, to 0.45 h^{-1}, around 75 mol % 2,5-xylenol and around 35 mol % phenol conversion is obtained on H-BEA-25 compared to around 70 mol % 2,5-xylenol and around 12 mol % phenol conversion on H-MFI-90.

On zeolite H-MOR-90 conversions are generally lower. Around 60 mol % 2,5-xylenol and around 25 mol % phenol conversion are obtained at a space velocity of 0.113 h^{-1}. Around 55 mol % and 20 mol % 2,5-xylenol and phenol conversions, respectively, are obtained at a space velocity of 0.225 h^{-1} and around 50 mol % and around 10 mol % 2,5-xyenol and phenol conversions, respectively, are obtained at the highest space velocity applied of 0.45 h^{-1}.

It appears that over all of the catalysts conversion of phenol declines steeper than conversion of 2,5-xylenol with increasing space velocity.

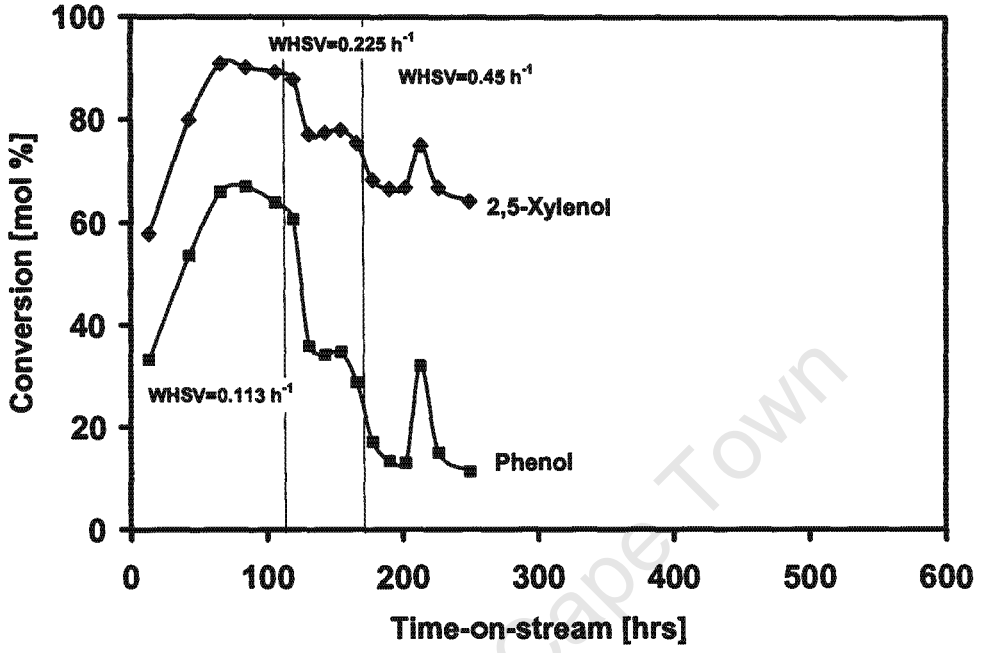


Figure 5-15 (Experiment 5): Conversion versus time-on-stream over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

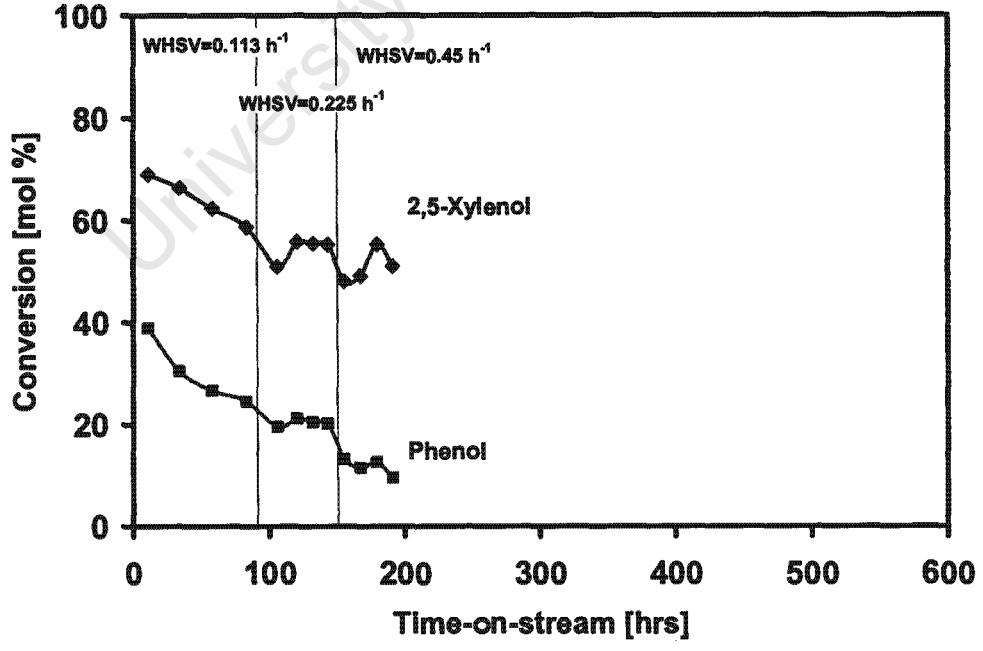


Figure 5-16 (Experiment 4): Conversion versus time-on-stream over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

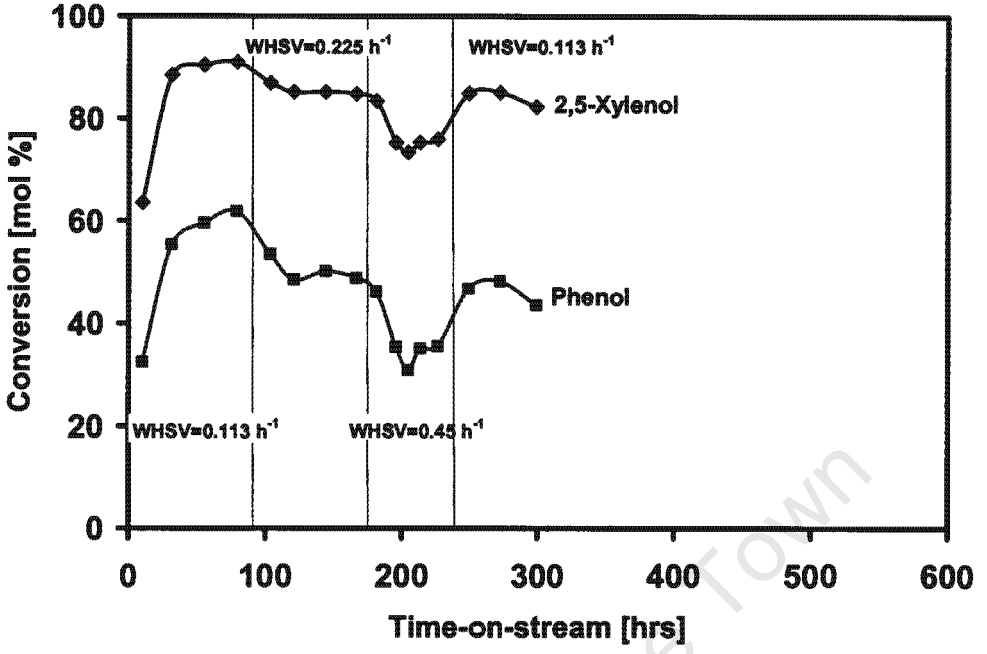


Figure 5-17 (Experiment 3): Conversion versus time-on-stream over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

Figures 5-18 to 5-20 show that for all of the three catalysts, selectivity increases with increasing 2,5-xylenol conversion for all product fractions except for the other xylenol isomers, the trimethylphenols and the ethers. At the same 2,5-xylenol conversion (say 70 mol %, indicated by a dotted vertical line in figures 5-18 to 5-20) similar selectivities for cresols (ca. 50 mol %) and other xylenol isomers (ca. 30 mol %) are obtained on zeolites H-MOR-90 and zeolite H-BEA-25 while lower cresol (only ca. 30 mol %) and higher other xylenol isomers (ca. 50 mol %) selectivities are obtained on zeolite H-MFI-90. The three zeolites show similar selectivities for lights and ethers, which are all below 10 mol % but differ in trimethylphenols selectivity which is around 10 mol % on H-BEA-25 zeolite and which is significantly higher over H-MOR-90 and H-MFI-90. Catalysts differ in similar manner in the selectivities of heavies, where zeolite H-MFI-90 shows the highest selectivity of ca. 15 mol % compared to H-BEA-25 and H-MOR-90 with less than 10 mol %.

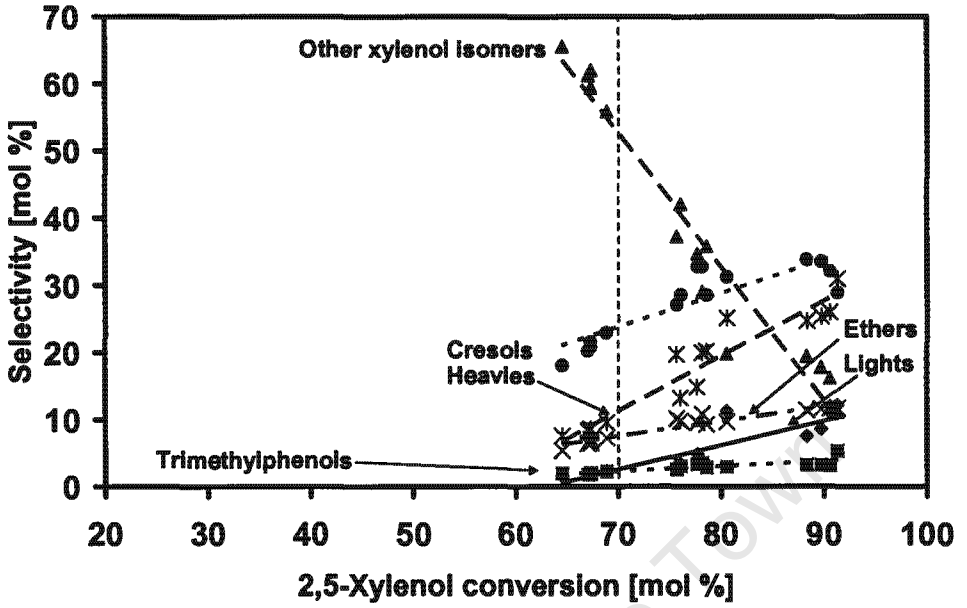


Figure 5-18 (Experiment 5): Selectivity versus 2,5-xylenol conversion over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350 °C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

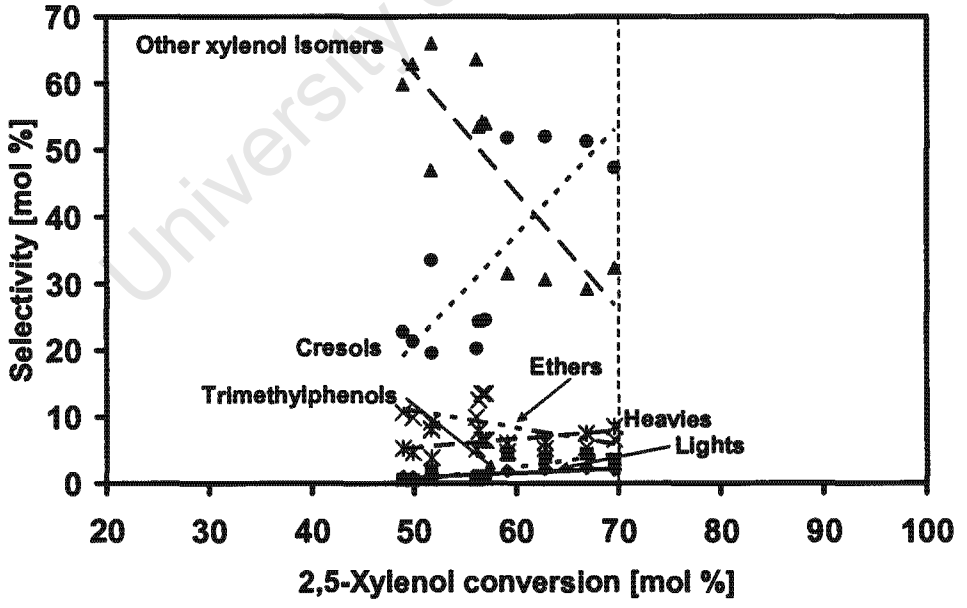


Figure 5-19 (Experiment 4): Selectivity versus 2,5-xylenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350 °C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

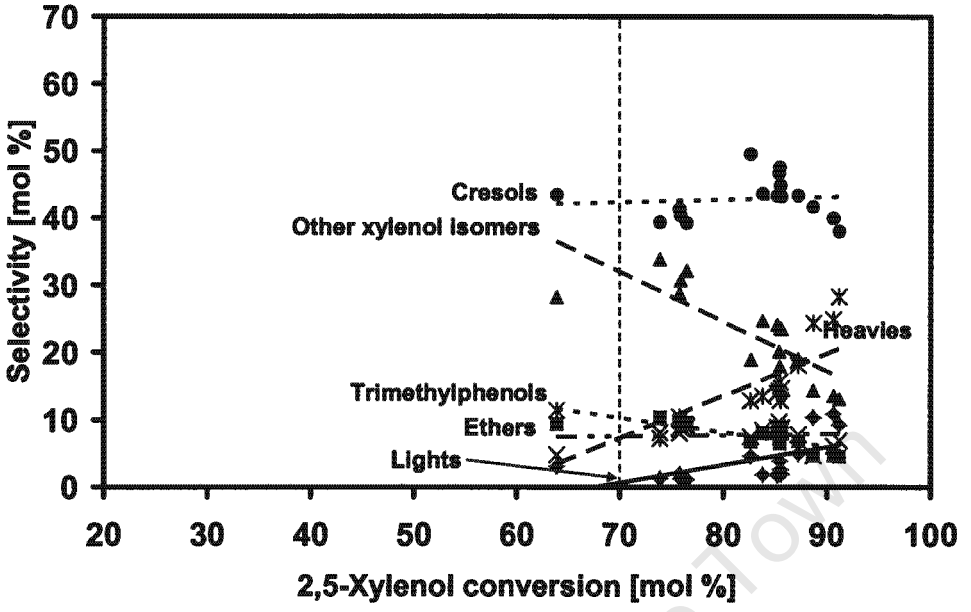


Figure 5-20 (Experiment 3): Selectivity versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350 °C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

Figures 5-21 to 5-23 show that yields of cresols, lights and heavies increase rather steeply with increasing 2,5-xylenol conversion for all of the three zeolites while the yields of ethers and trimethylphenols increase only slightly (H-MFI-90) or are almost constant (H-MOR-90 and H-BEA-25). High yields of cresols are obtained at e.g. 70 mol % 2,5-xylenol conversion on zeolites H-MOR-90 (ca. 30 mol %) and H-BEA-25 (ca. 25 mol %) compared to H-MFI-90 (only ca. 10 mol %) at the same 2,5-xylenol conversion. Similar yields of other xylenol isomers (ca. 18 mol %) are obtained at 70 mol % 2,5-xylenol conversion over zeolites H-MOR-90 and H-BEA-25, while a higher yield (ca. 25 mol %) is obtained on zeolite H-MFI-90 at the same conversion. Yields of the other fractions over all catalysts are below 10 mol % at 70 mol % 2,5-xylenol conversion.

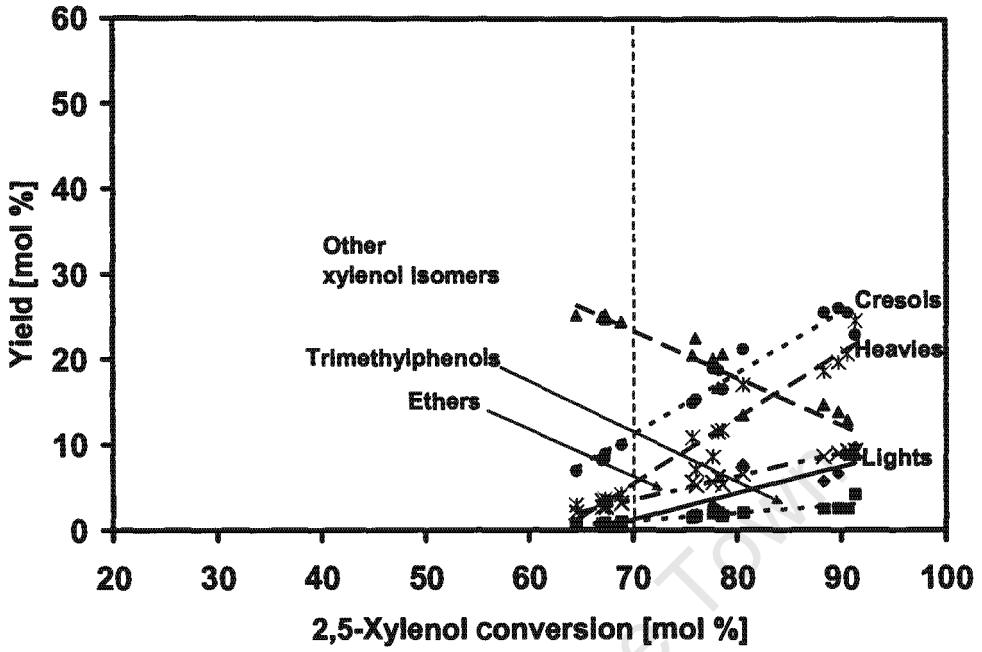


Figure 5-21 (Experiment 5): Yield versus 2,5-xylenol conversion over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350 °C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

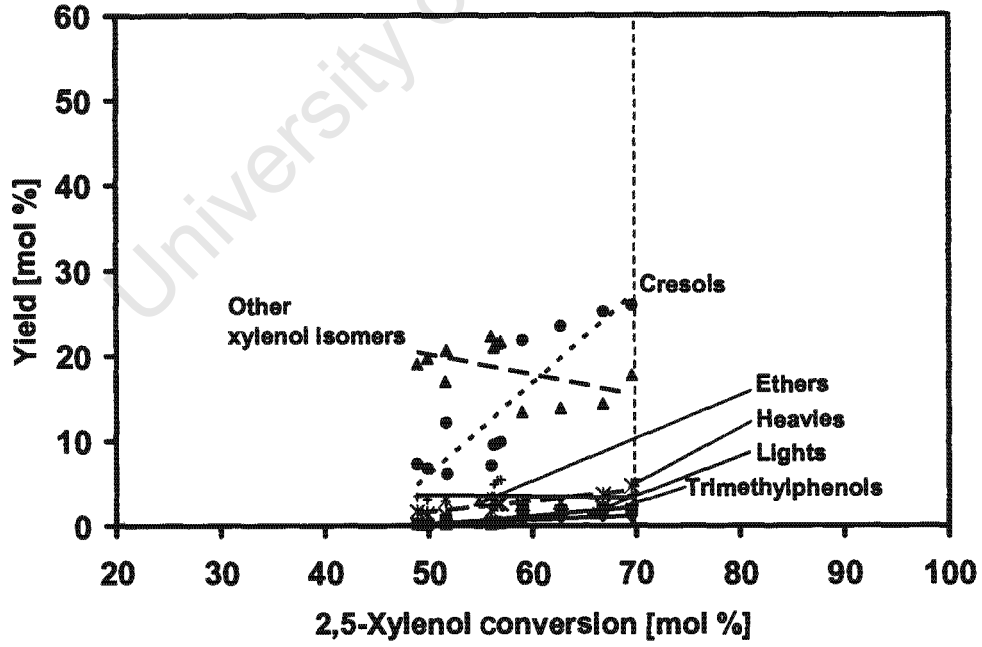


Figure 5-22 (Experiment 4): Yield versus 2,5-xylenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

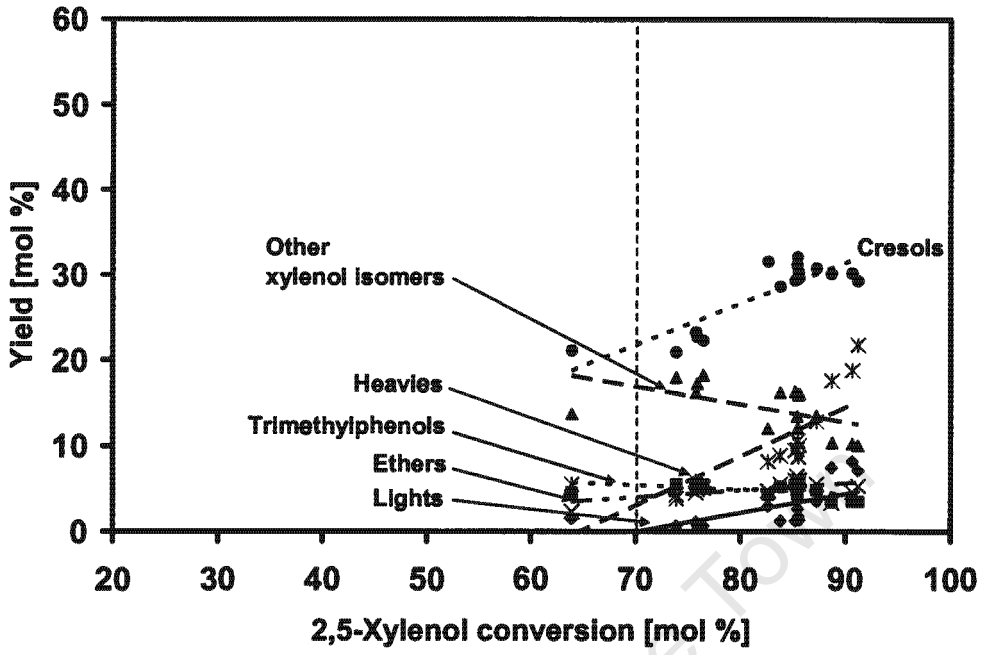


Figure 5-23 (Experiment 3): Yield versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

5.4.1 Catalyst of choice

Based on the comparison of catalysts described above, a decision was made towards the catalyst with which the experimental work had to continue. Of the three catalysts compared, H-MFI-90 showed the lowest selectivity towards the desired product, cresol, but the highest towards undesired heavies and lights.

Of the two remaining catalysts, H-BEA-25 and H-MOR-90, the activity of the latter appeared to continually decline with time-on-stream, while the activity of H-BEA-25 appeared rather stable.

Consequently, catalyst H-BEA-25 was chosen for further studies.

5.5 Effect of reaction conditions

The effects of changing the ratio of phenol to 2,5-xylenol in the feed, space velocity and reaction temperature were studied over catalyst H-BEA-25 on the basis of conversion, selectivity and yield. The results obtained are presented in sections 5.4 and 5.5.1 to 5.5.3.

5.5.1 Effect of phenol to 2,5-xylenol ratio

To study the effect of the phenol to 2,5-xylenol ratio, experiments were carried out with 1 : 1, 5 : 1 and 20 : 1 molar ratio feed mixtures of phenol and 2,5-xylenol at a temperature of 350°C. Figures 5-17, 5-20 and 5-23 show the results obtained for 1 : 1 molar ratio, figures 5-24 to 5-34 those for the higher ratios and also the average values versus ratio.

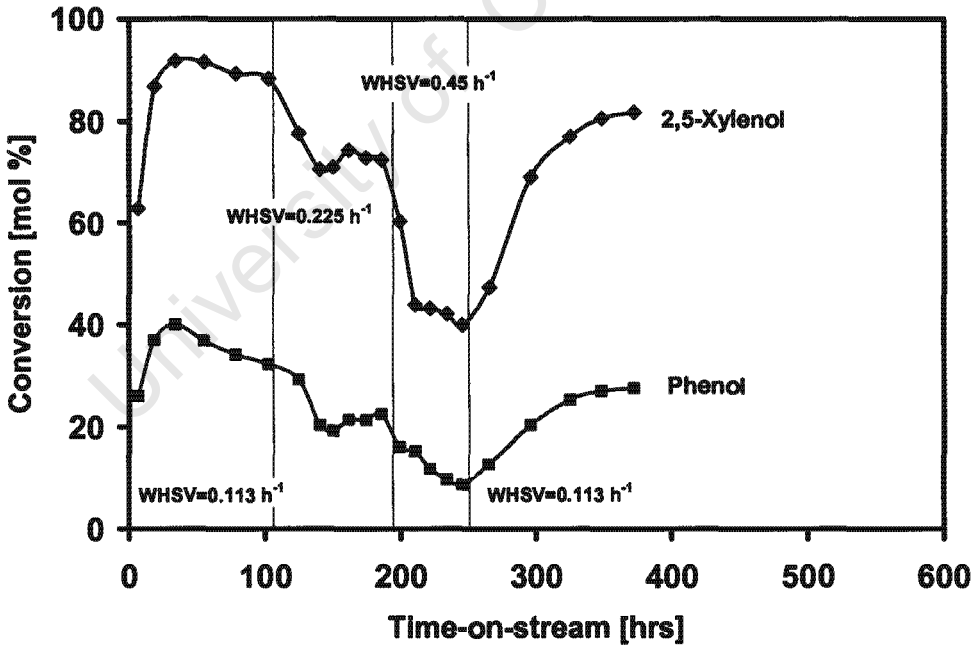


Figure 5-24 (Experiment 7): Conversion versus time-on-stream over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

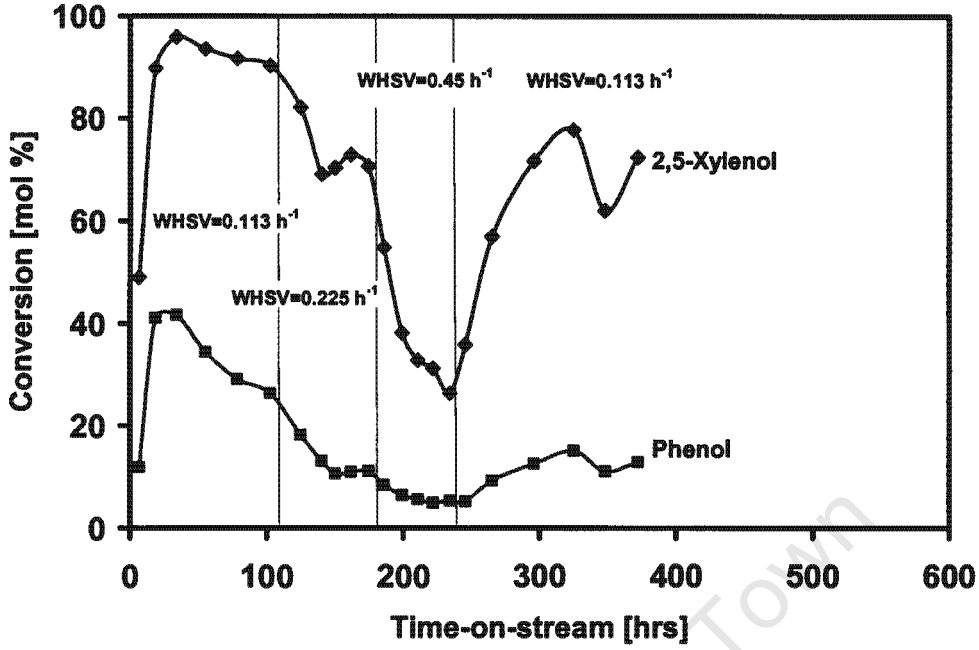


Figure 5-25 (Experiment 8): Conversion versus time-on-stream over H-BEA-25 catalyst for a 20 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

Figures 5-17, 5-24 and 5-25 compared, show that phenol and 2,5-xylenol conversions decrease with increasing phenol : 2,5-xyenol molar ratio. This can be seen at a space velocity of 0.113 h^{-1} (using data from the repeat experiment at the longest time-on-stream in figure 5-25) where the phenol conversion declines from ca. 40 mol % for a molar ratio of 1 : 1 through 30 mol % for a molar ratio of 5 : 1, to some 15 mol % for a molar ratio of 20 : 1. The same trend is seen at the space velocities of 0.225 and 0.45 h^{-1}. At space velocities of 0.113 h^{-1} (repeat data) and 0.225 h^{-1}, 2,5-xylenol conversion is only slightly declining from ca. 85 mol % for a phenol and 2,5-xylenol molar ratio of 1 : 1 to ca. 75 mol % for a ratio of 20 : 1. At the highest WHSV of 0.45 h^{-1} rather low values are obtained.

The above is summarised in figures 5-26 and 5-27 where the average conversions are plotted against the phenol to 2,5-xylenol ratio. Average conversion was determined by calculating the average of the data points obtained at each space velocity after stabilization (repeat data for the space velocity = 0.113 h^{-1}).

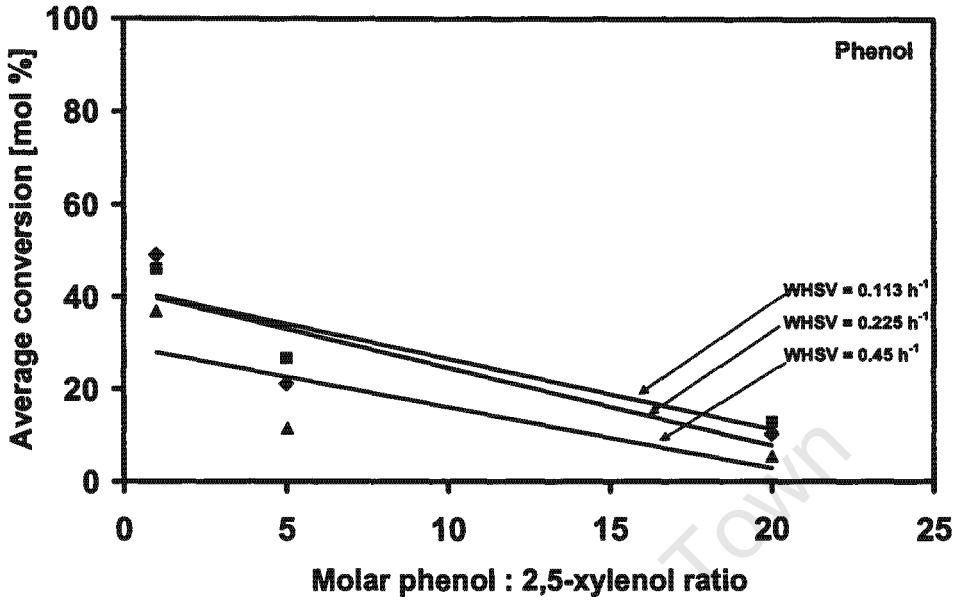


Figure 5-26 (Experiments 3, 7 and 8): Average conversion of phenol versus the molar ratio in feed mixtures of phenol and 2,5-xylenol over H-BEA-25 catalyst at a temperature of 350°C and different space velocities (WHSV)

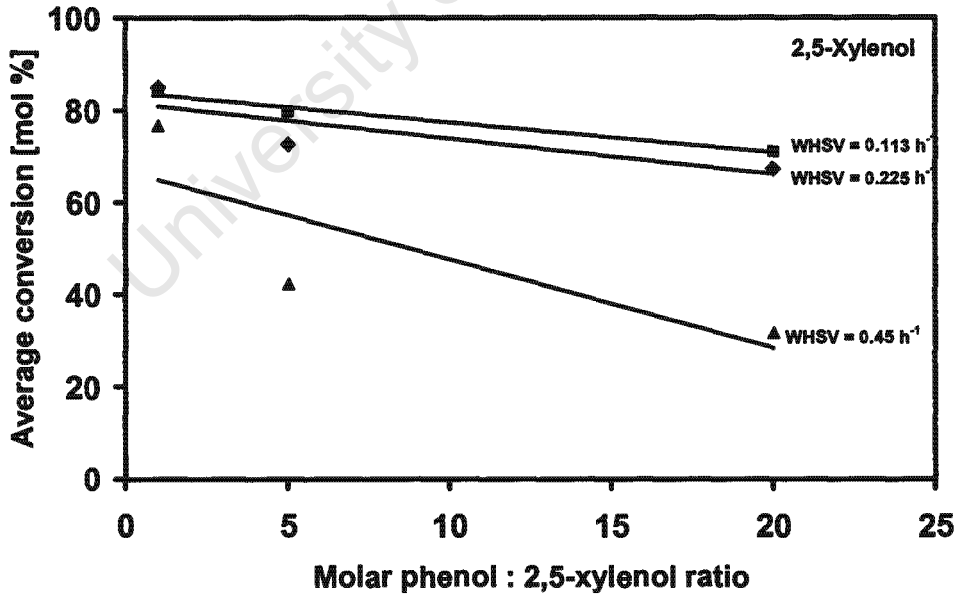


Figure 5-27 (Experiments 3, 7 and 8): Average conversion of 2,5-xylenol versus the molar ratio in feed mixtures of phenol and 2,5-xylenol over H-BEA-25 catalyst at a temperature of 350°C and different space velocities (WHSV)

While the conversion of phenol declines from 30 – 40 mol% to almost a quarter when increasing the molar phenol : 2,5-xylenol ratio from 1 : 1 to 20 : 1, the response of the conversion of 2,5-xylenol is less pronounced especially at the low space velocities of 0.113 h^{-1} and 0.225 h^{-1}. The data obtained from the highest space velocity of 0.45 h^{-1} appear to be flawed by scatter.

Figures 5-20, 5-28 and 5-29 show that similar trends are obtained as a function of 2,5-xylenol conversion for all phenol to 2,5-xylenol ratios, however, levels of individual selectivities of product classes are not significantly different. It should be noted that data from short time-on-stream, i.e. the first period of operating at a space velocity of 0.113 h^{-1} are included in all of the three figures (highest conversion data points).

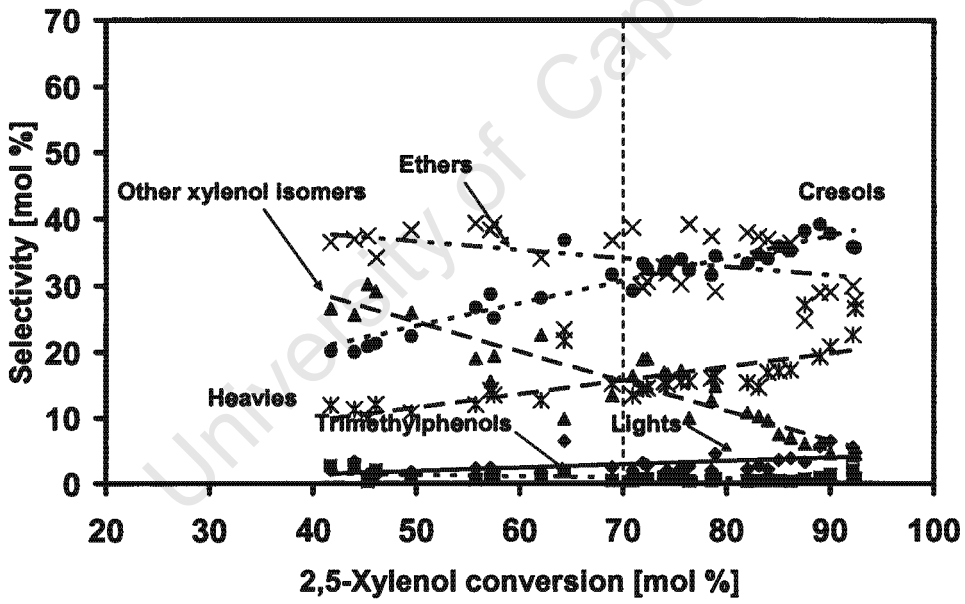


Figure 5-28 (Experiment 7): Selectivity versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

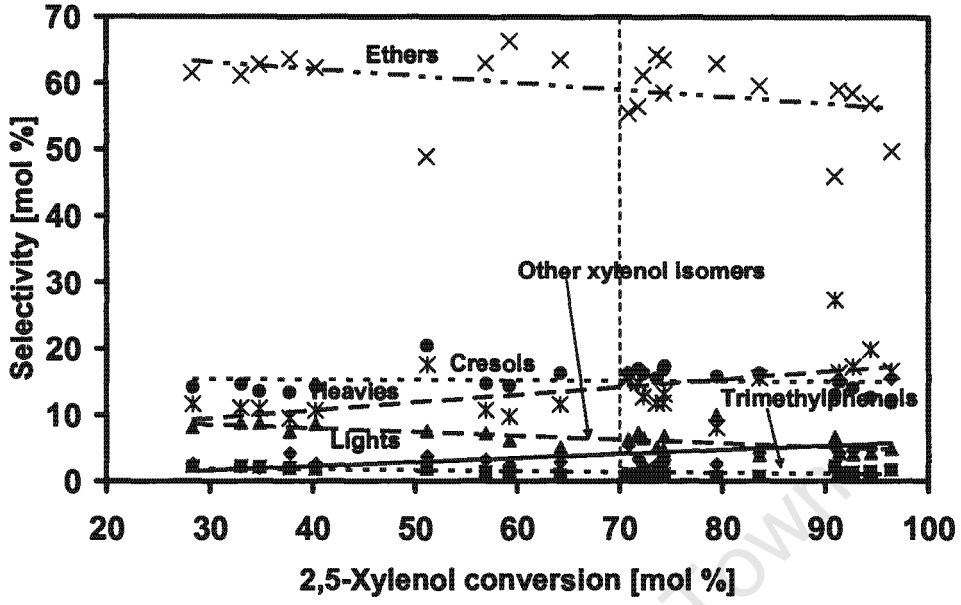


Figure 5-29 (Experiment 8): Selectivity versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 20 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

Figure 5-30 summarises these results in the form of average selectivies. Average selectivities consider only data that were obtained after stabilisation. Figure 5-30 shows for the medium space velocity of 0.225 h^{-1} as an example that with increasing phenol to 2,5-xylenol ratio, steeply increasing average selectivities for ethers and, particularly, constant selectivities for lights and heavies are obtained, while the average selectivities for cresols, other xylenol isomers and trimethylphenols decrease.

For the yields similar trends are obtained with increasing phenol to 2,5-xylenol molar ratio (figures 5-23, 5-31 and 5-32). As a function of 2,5-xylenol conversion all yields except that of other xylenol isomers at 1 : 1 and 5 : 1 molar phenol to 2,5-xylenol ratio increase or are more or less constant. Figure 5-33, the summary of these results, shows that on average yields of all product fractions decrease with increasing phenol to 2,5-xylenol molar ratio with the only exception of ethers whose yields are more or less constant. The average yields considered only data that were obtained after stabilisation.

A survey of figures 5-26, 5-27, 5-30 and 5-33 suggests that results for the 5 : 1 molar ratio feed mixture are to some extent outliers.

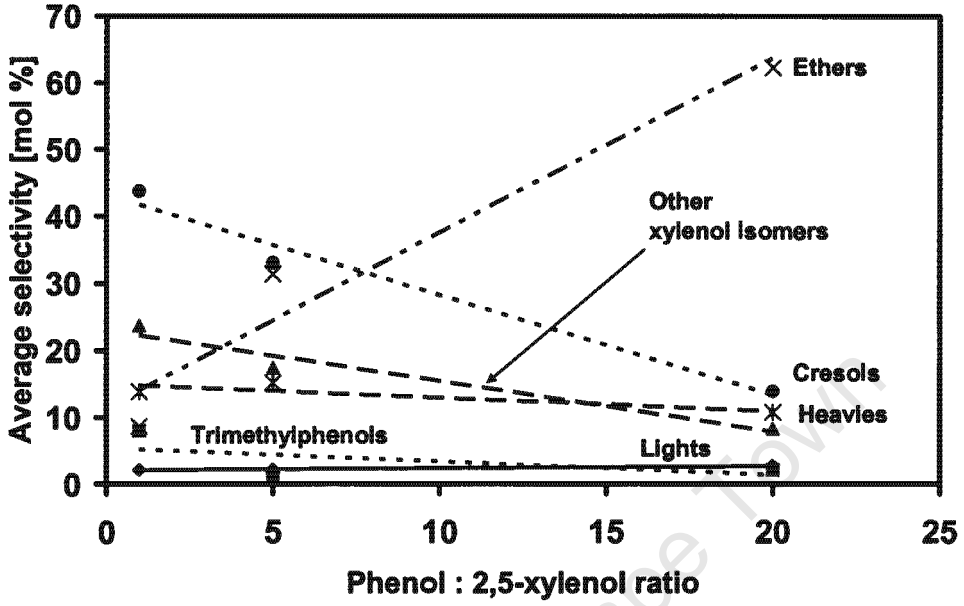


Figure 5-30 (Experiments 3, 7 and 8): Average selectivity versus the molar ratio of feed mixtures of phenol and 2,5-xylenol over H-BEA-25 catalyst at a temperature of 350°C and a space velocity (WHSV) of 0.225 h^{-1}

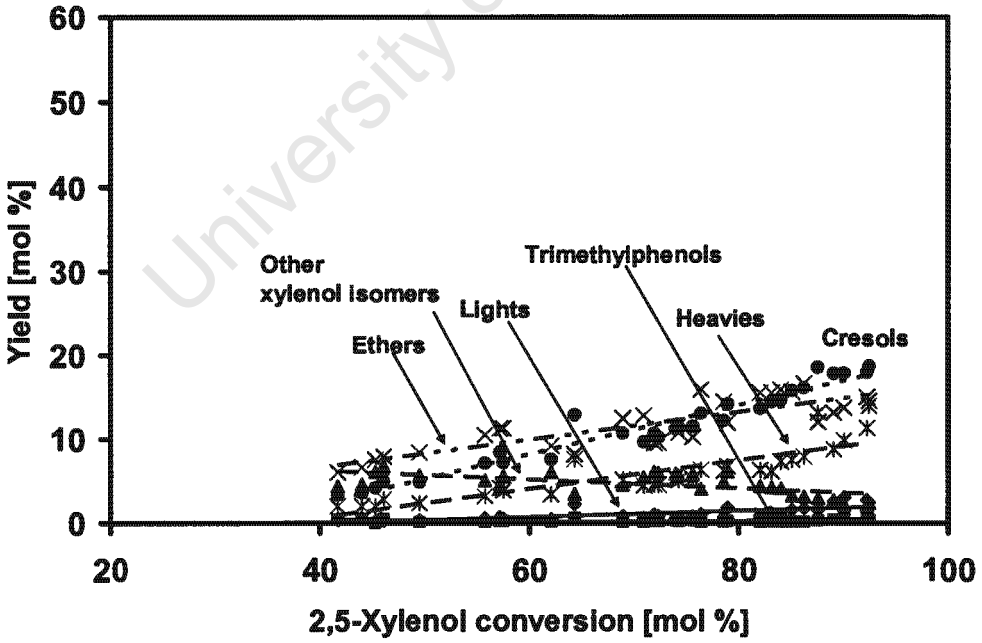


Figure 5-31 (Experiment 7): Yield versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

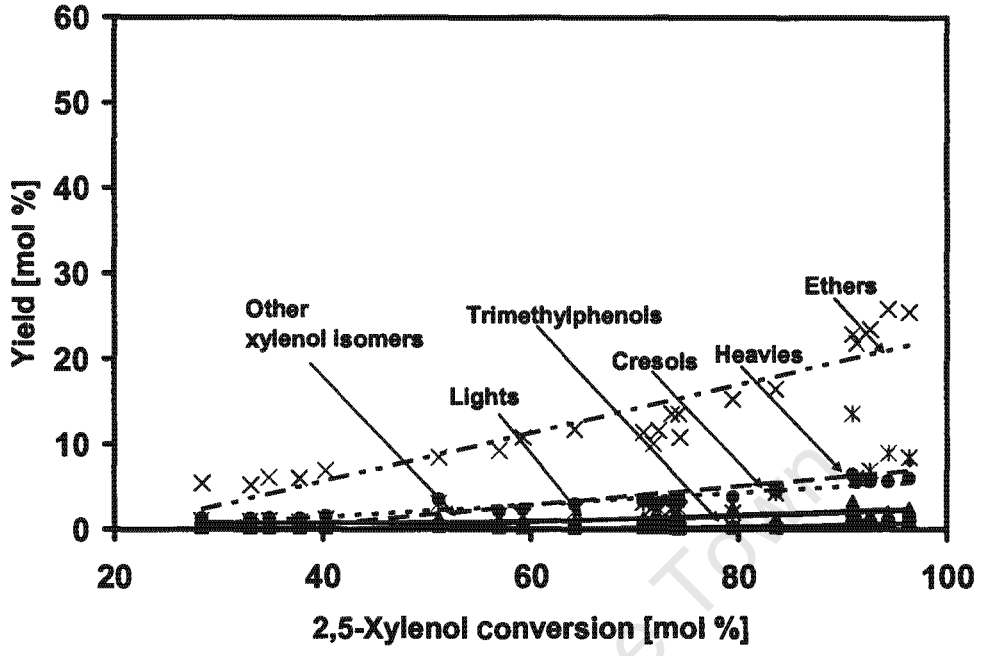


Figure 5-32 (Experiment 8): Yield versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 20 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

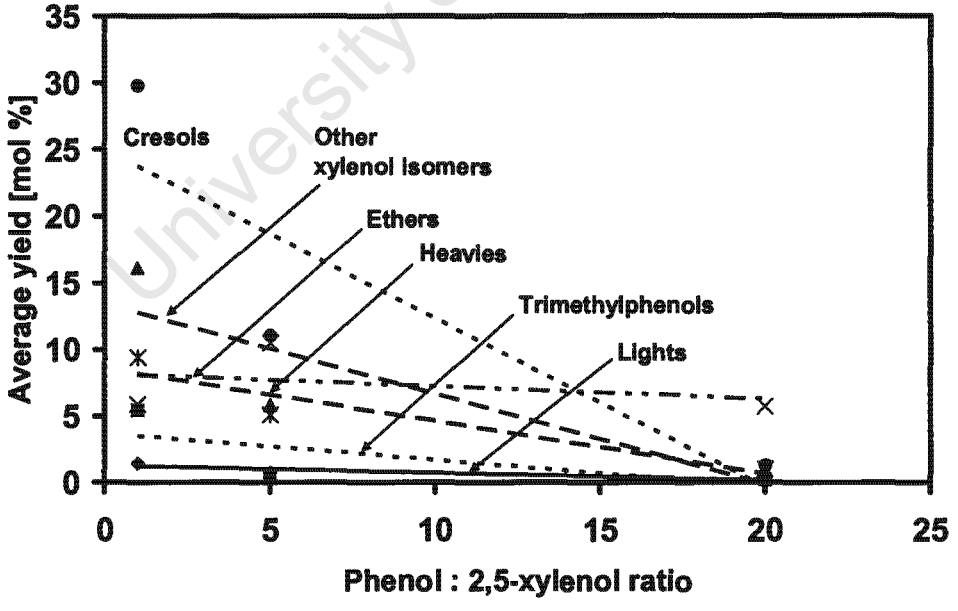


Figure 5-33 (Experiments 3, 7 and 8): Average yield versus the molar ratio of feed mixtures of phenol and 2,5-xylenol over H-BEA-25 catalyst at a temperature of 350°C and a space velocity (WHSV) of 0.23 h^{-1}

5.5.2 Effect of space velocity

To study the effect of space velocity, experiments were carried out over all the three zeolite catalysts of interest (H-MFI-90, H-MOR-90 and H-BEA-25) for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C. The primary results obtained have been presented in figures 5-15 to 5-17 as conversion versus time-on-stream plots and in figures 5-18 to 5-23 as selectivities and yields, respectively, versus 2,5-xylenol conversion plots. In figures 5-34 to 5-42 the averages of data points obtained at stabilised operation at each space velocity are plotted for conversion, selectivity and yield.

Figures 5-34 to 5-36 show that conversions decrease with increasing space velocity over all the three catalysts. This was also shown in figures 5-15 to 5-17 where individual data points on conversion are plotted against time-on-stream at different space velocities.

According to both sets of figures 5-15 to 5-17 and 5-34 to 5-36 the effect of space velocity is stronger on phenol conversion, which declines faster, relatively, when space velocity increases.

Figures 5-37 to 5-42 show that similar trends are obtained for both selectivity and yield for each catalyst when space velocity changes. Selectivity and yield for other xylenol isomers increase with increasing space velocity while the selectivities and yields for all other product fractions decrease with increasing space velocity over all the tested catalysts, the only exception being the trimethylphenols obtained on catalyst H-BEA-25 (see figures 5-39 and 5-42) whose selectivity and yield are more or less constant with increasing space velocity.

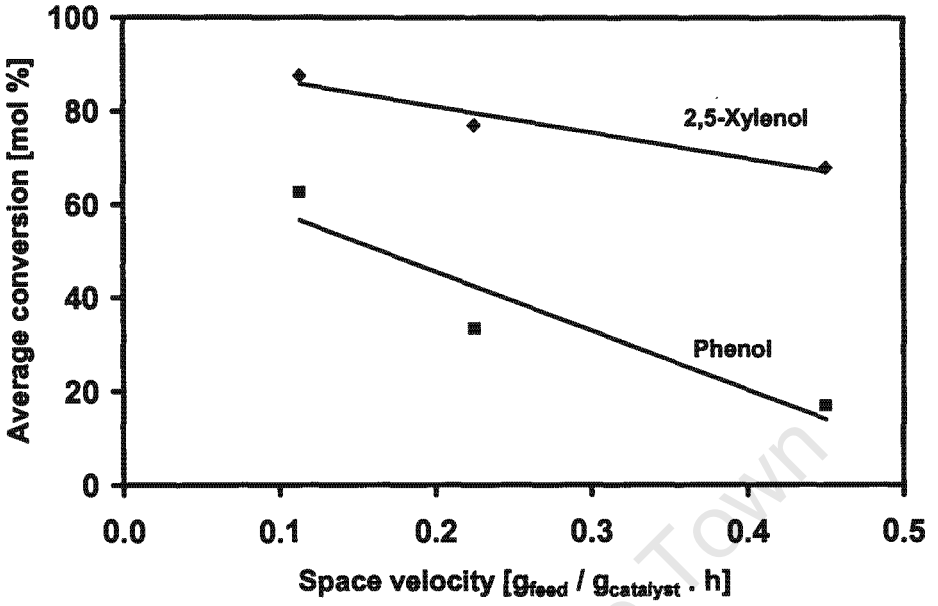


Figure 5-34 (Experiment 5): Average phenol and 2,5-xylenol conversion versus space velocity over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

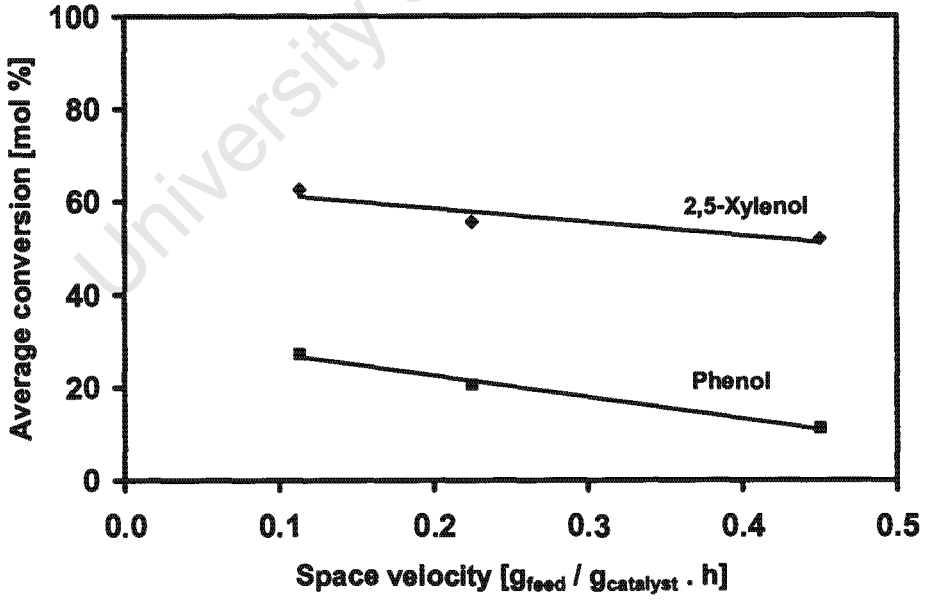


Figure 5-35 (Experiment 4): Average phenol and 2,5-xylenol conversion versus space velocity over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

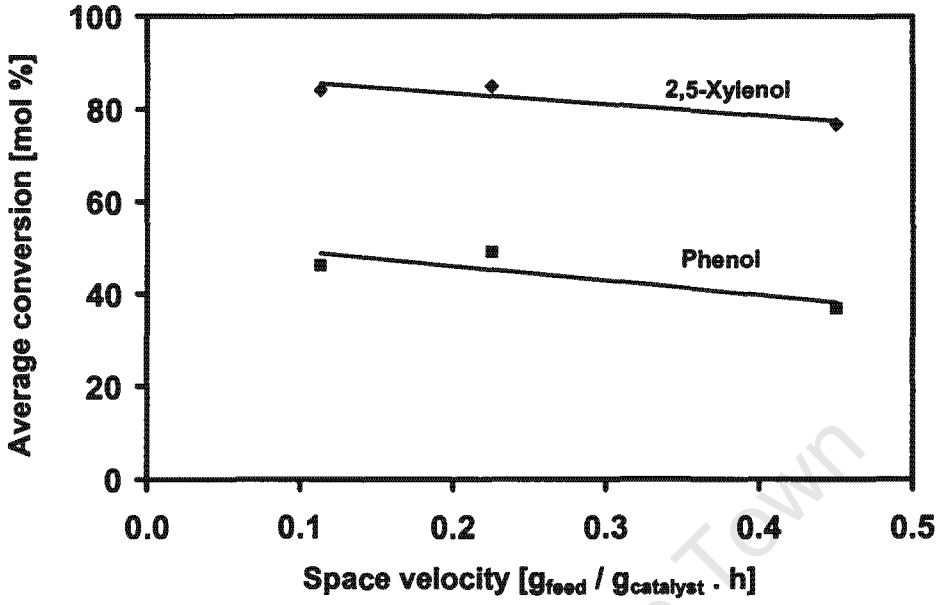


Figure 5-36 (Experiment 3): Average phenol and 2,5-xylenol conversion versus space velocity over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

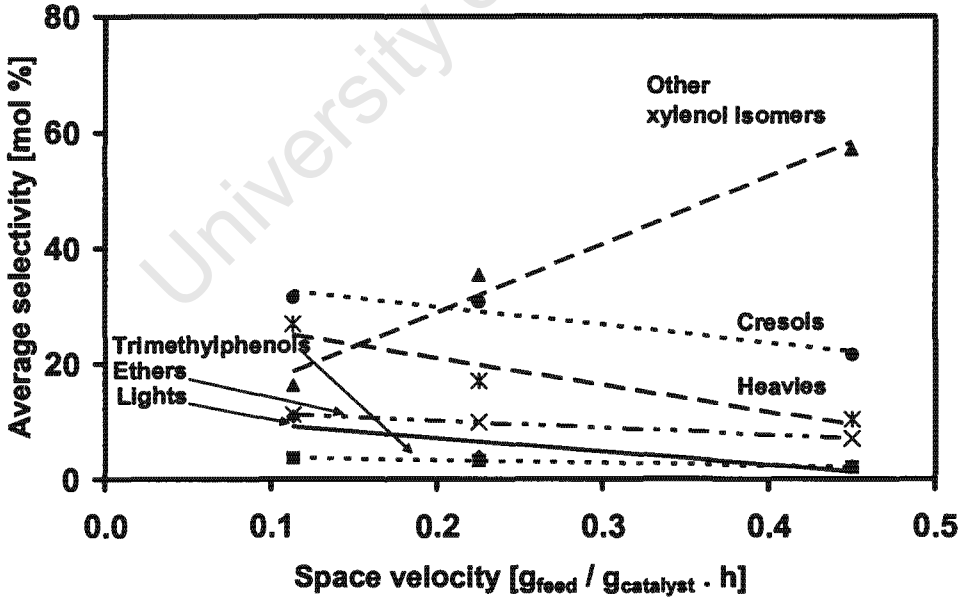


Figure 5-37 (Experiment 5): Average selectivity versus space velocity over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

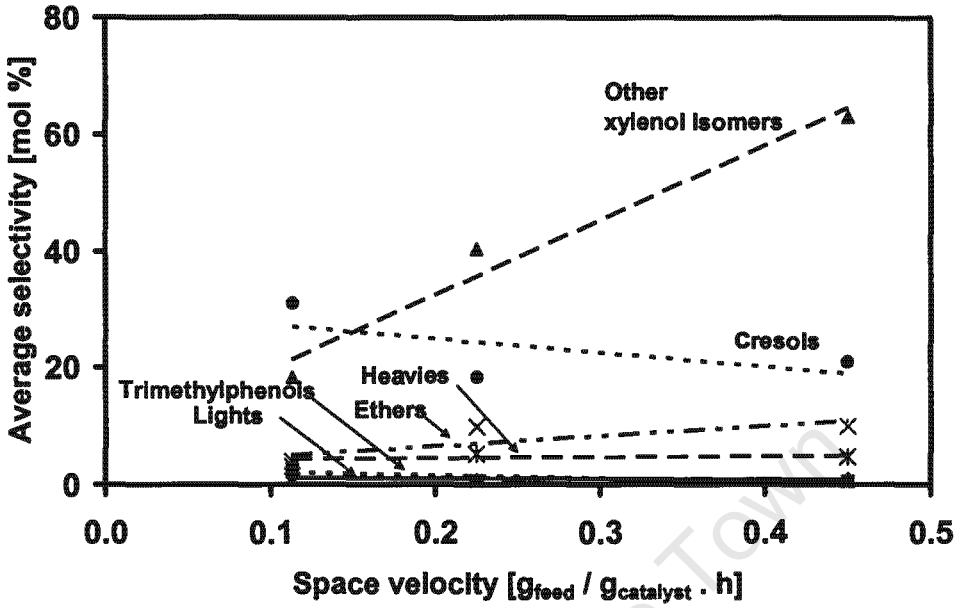


Figure 5-38 (Experiment 4): Average selectivity versus space velocity over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

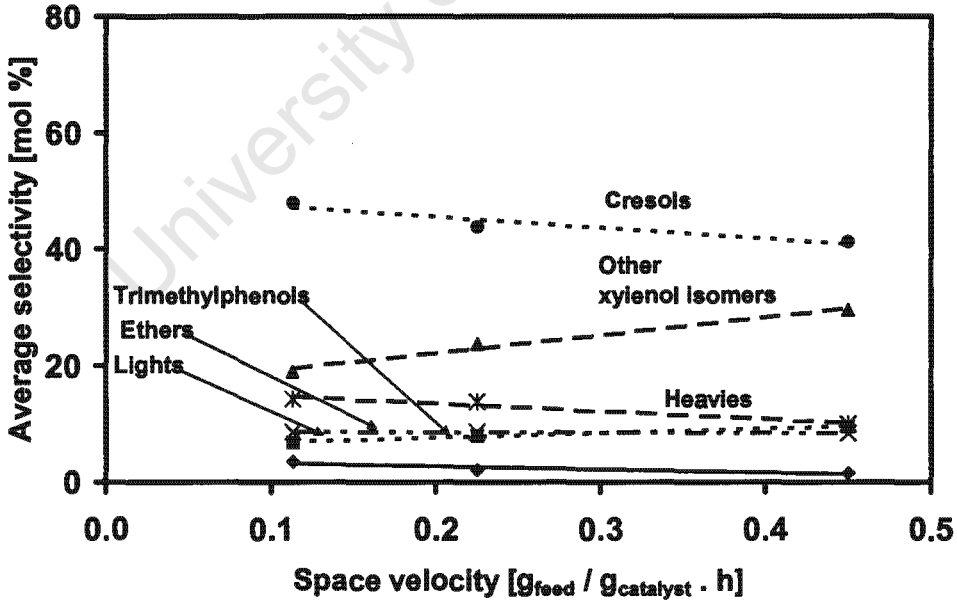


Figure 5-39 (Experiment 3): Average selectivity versus space velocity over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

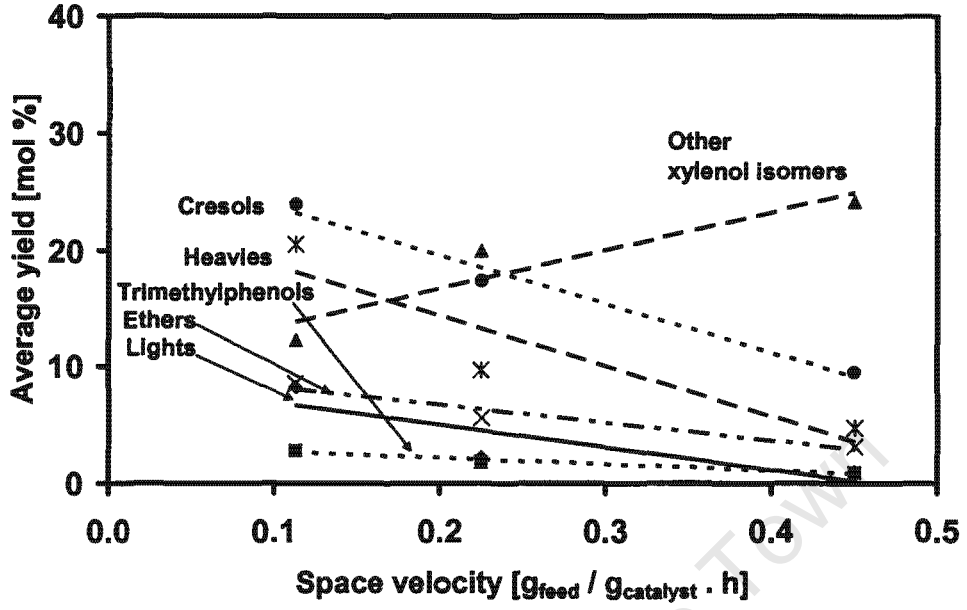


Figure 5-40 (Experiment 5): Average yield versus space velocity over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

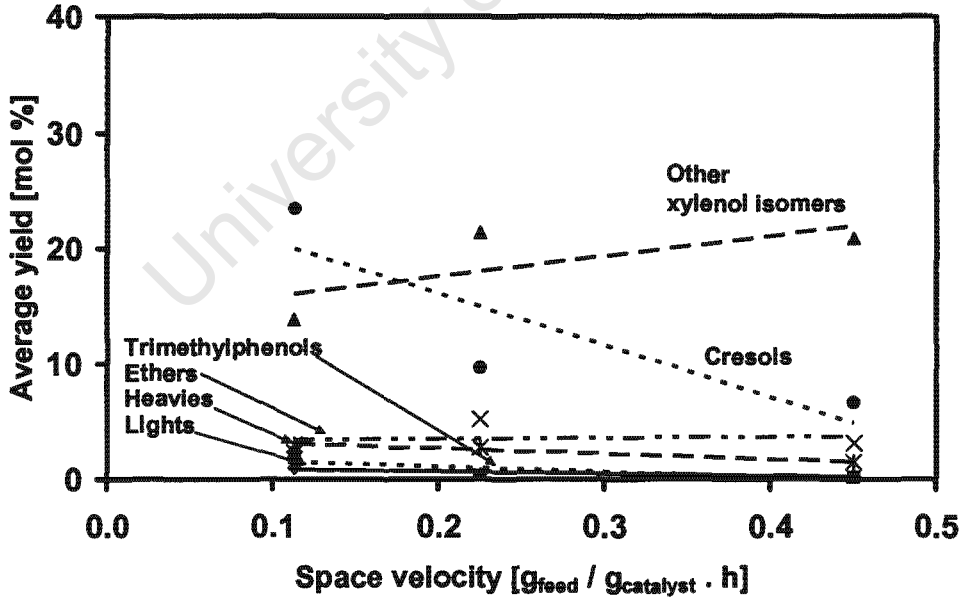


Figure 5-41 (Experiment 4): Average yield versus space velocity over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

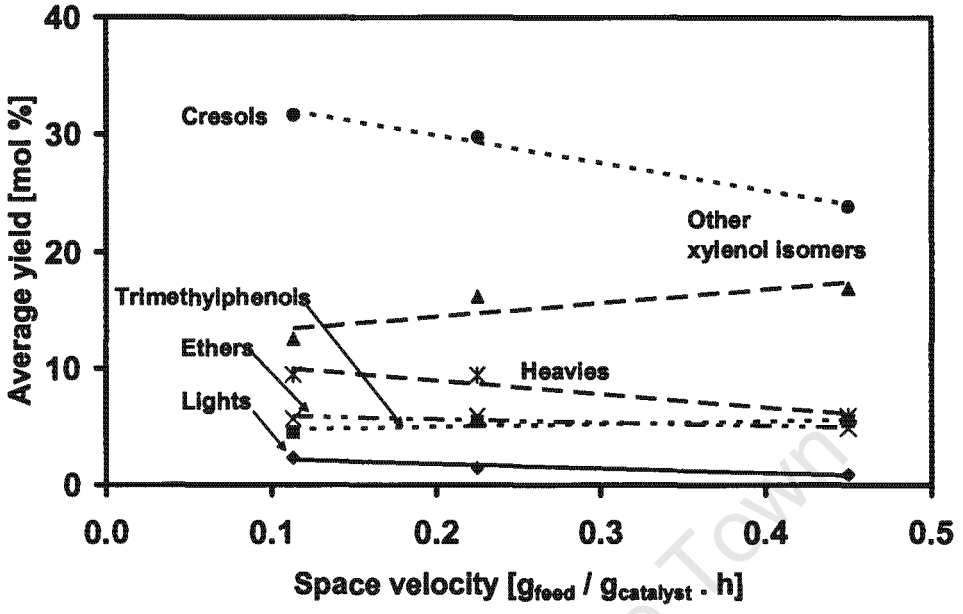


Figure 5-42 (Experiment 3): Average yield versus space velocity over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C

5.5.3 Effect of temperature

To study the effect of temperature, temperature was varied over H-BEA-25 catalyst in 50°C steps between 250°C and 450°C in two of the initial experiments with 1 : 1 molar ratio feed and in 25°C steps around 350°C, i.e. in the optimum temperature range (see section 5.1) at the end of a space velocity series experiment where a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol was used.

The primarily obtained results, plotted versus time-on-stream are shown in figures 5-1, 5-2 and 5-43.

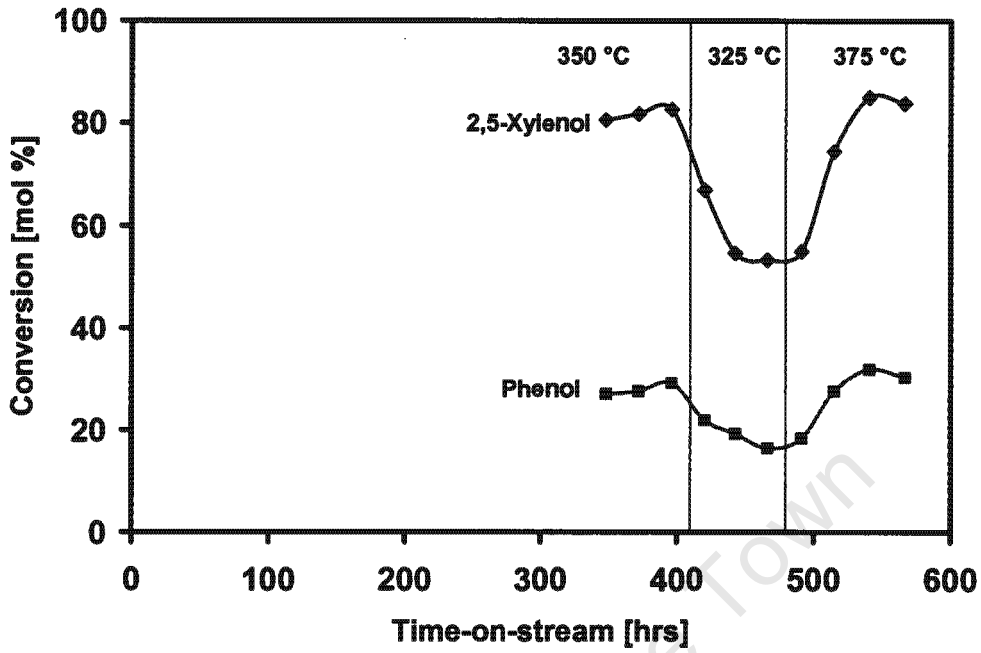


Figure 5-43 (Experiment 7): Conversion versus time-on-stream over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.113 h^{-1}

All figures show that conversion increases with increasing temperature except at the highest temperature, 450°C (figure 5-2), when catalyst deactivation effects appear to start playing a significant role.

Average conversions, selectivities and yields for the 250 to 450°C series of experiments with the 1 : 1 molar phenol : 2,5-xylenol mixture as the feed have been shown in figures 5-3 to 5-5 and described in section 5.1. For the 325 to 375°C series with the 5 : 1 molar phenol : 2,5-xylenol feed mixture these are shown in figures 5-44 to 5-46.

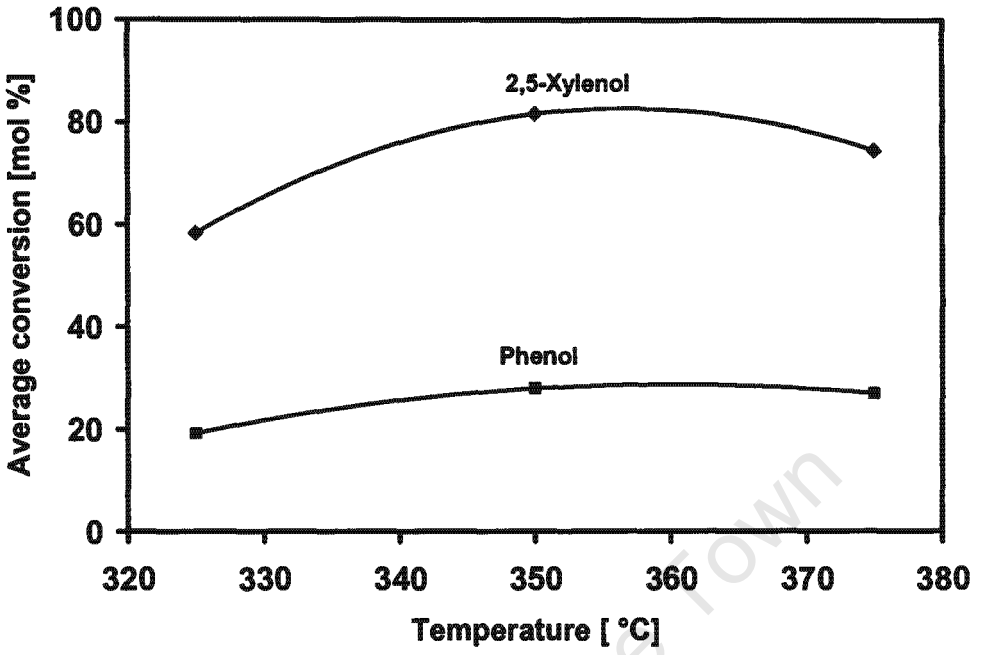


Figure 5-44 (Experiment 7): Average phenol and 2,5-xylenol conversion versus temperature over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.113 h^{-1}

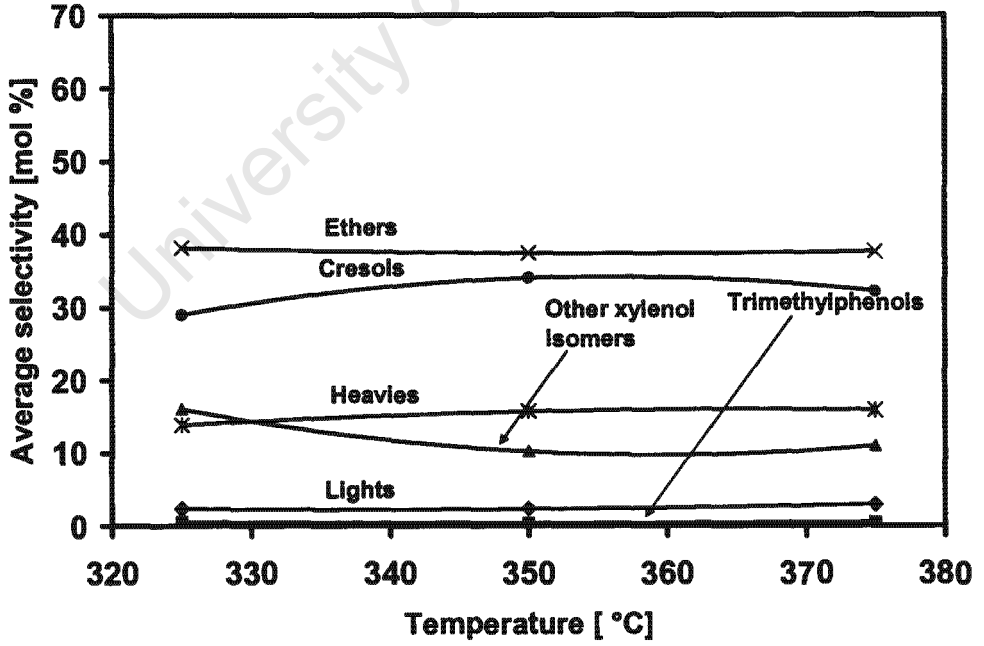


Figure 5-45 (Experiment 7): Average selectivity versus temperature over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.113 h^{-1}

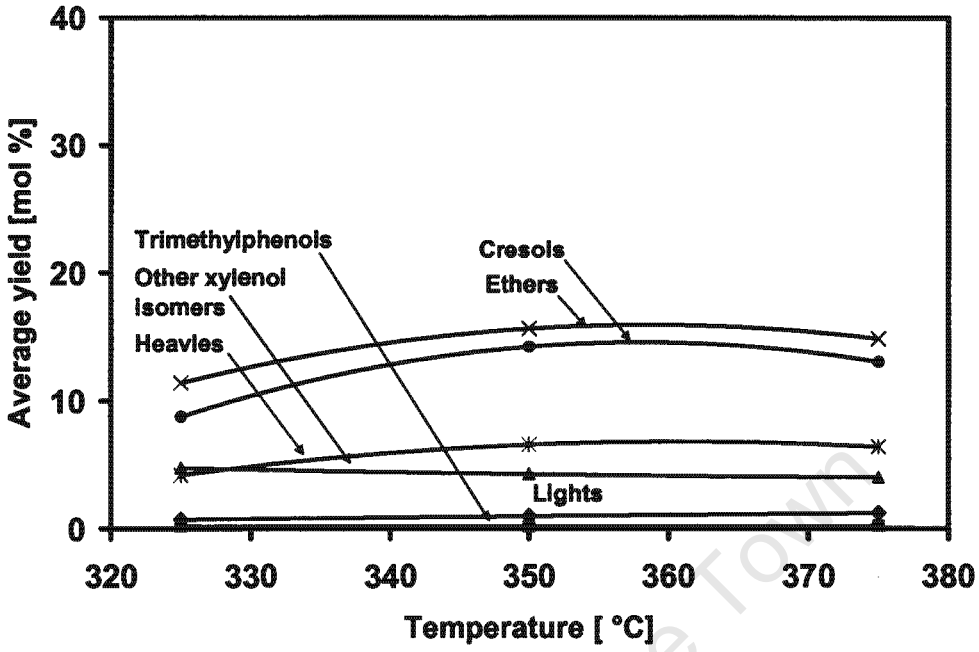


Figure 5-46 (Experiment 7): Average yield versus temperature over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a space velocity (WHSV) of 0.113 h^{-1}

Results are similar to those obtained for the first series. Conversion increases with increasing temperature and passes over a maximum at around 375°C as is showing in figure 5-3. So do the selectivity and yield of cresols, while those for the other xylenol isomers decline (all corresponding to the results of the first temperature series as shown in figures 5-4 and 5-5).

5.6 Reactor effluent for the reaction of 2,5-xylenol and phenol

The composition of the reactor effluent from reacting the 1 : 1 molar phenol to 2,5-xylenol feed mixtures on the three zeolite catalysts of interest is shown in figures 5-47 to 5-49. "Reactor effluent" comprises all products, so that this data is identical to what has already been shown as "yields" in figures 5-21 to 5-23, but includes also the unconverted feed compounds, namely phenol and 2,5-xylenol, whose contents are steeply declining with increasing conversion.

From these 1 : 1 molar feed mixtures there is always much more phenol remaining than 2,5-xylenol. For instance at 70 mol % 2,5-xylenol conversion, when only 15 mol % of feed 2,5-xylenol is left in the reactor effluent (note that the feed mixture consisted of only 50 mol% 2,5-xylenol), the phenol content is still at around 35 mol % with H-MFI-90 and around 30 mol % with the other two catalysts. However, considering the 'other xylenols isomers' that have formed, the total xylenol content in the reactor effluent is almost equal to the phenol content (on a molar basis).

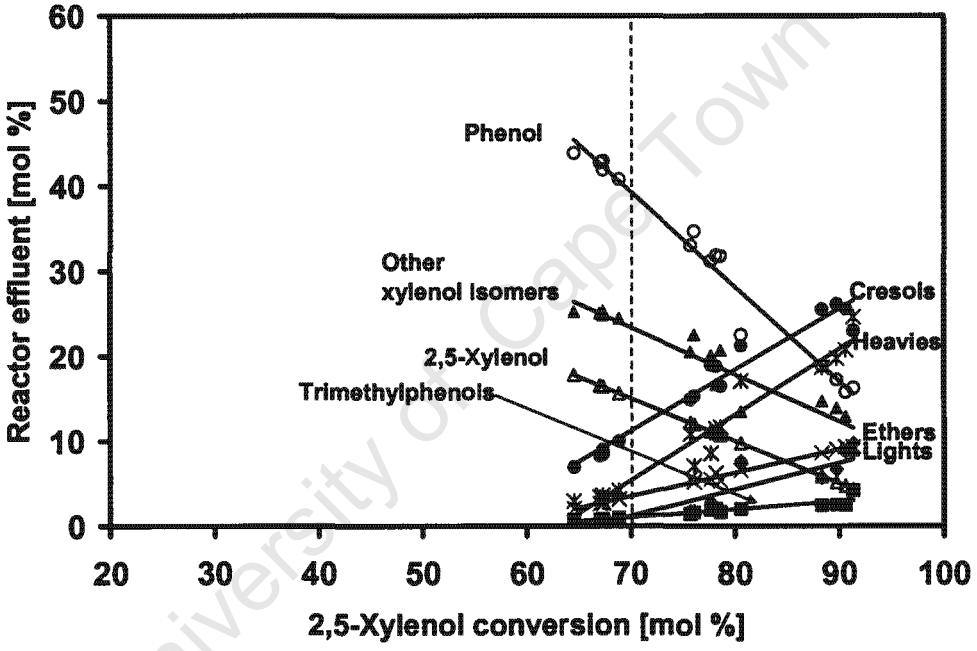


Figure 5-47 (Experiment 5): Reactor effluent versus 2,5-xylenol conversion over H-MFI-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and changing space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

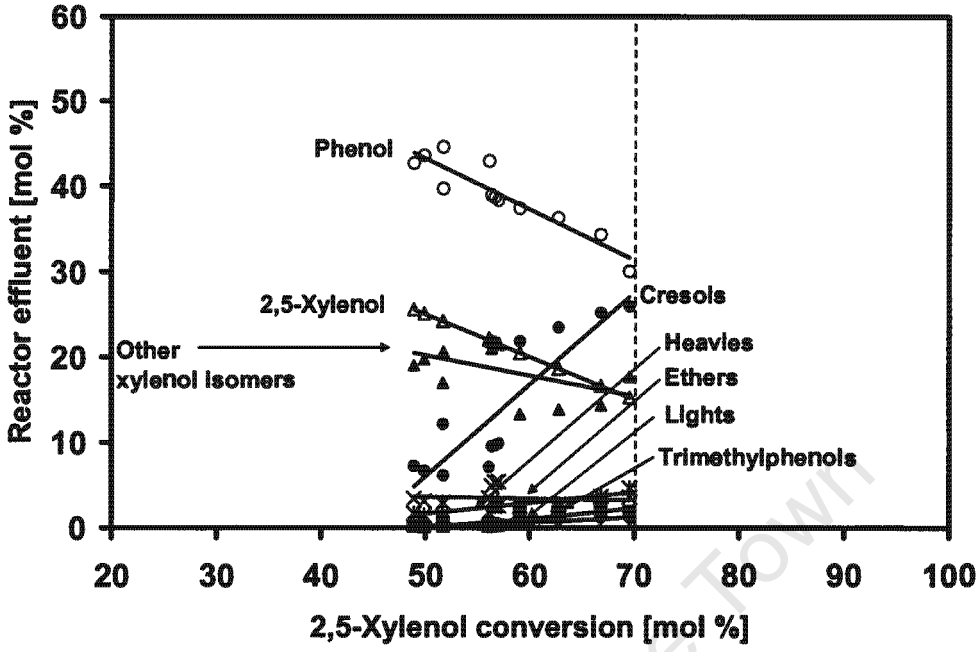


Figure 5-48 (Experiment 4): Reactor effluent versus 2,5-xylenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and changing space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

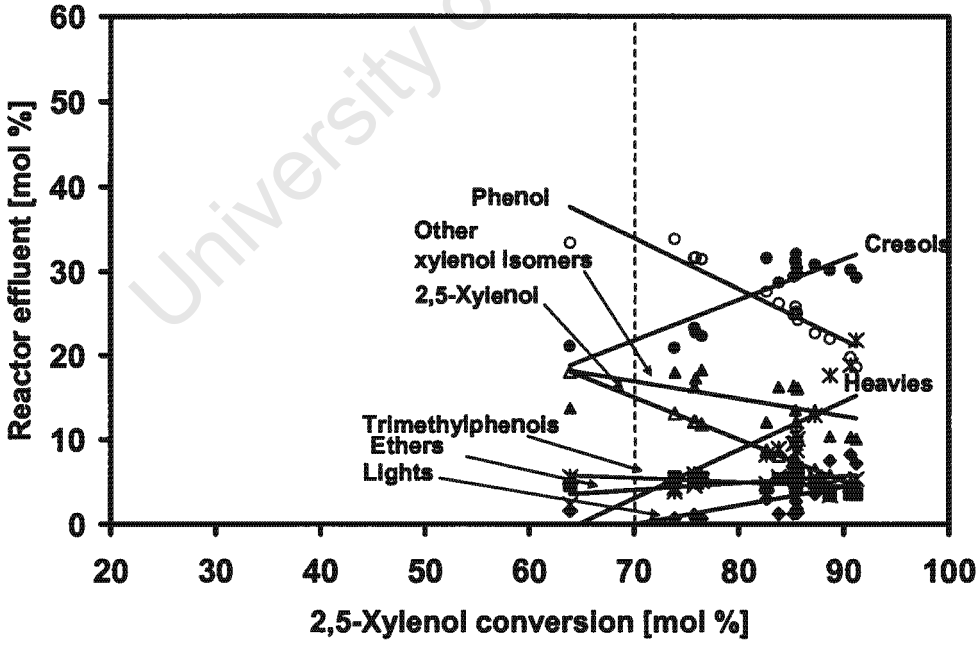


Figure 5-49 (Experiment 3): Reactor effluent versus 2,5-xylenol conversion over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and changing space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

5.7 Reaction of higher methylphenols with phenol

Experiments were carried out where 2,3,6-trimethylphenol and a simulated technical mixture, containing a multitude of higher methylphenols, were reacted with phenol.

5.7.1 Reaction of phenol with 2,3,6-trimethylphenol

An experiment was carried out with a 1 : 1 molar ratio feed mixture of phenol : 2,3,6-trimethylphenol at a temperature of 350°C and different space velocities. The results obtained are presented in figures 5-50 to 5-53. It should be noted that this experimental series was carried out over H-MOR-90 catalyst.

It should also be noted that the volume flow rates produced by the metering pump and, due to the effectively equal densities, the mass flow rates and WHSV of the phenol-with-2,5-xylenol and phenol-with-2,3,6-trimethylphenol mixtures were equal but not the molar flow rates, due to the higher molecular mass of the trimethylphenol. The molar flow rate of the latter, and thus the molar hourly space velocity was only 94 % of that of the former.

Figures 5-50 and 5-51 show that, as it is the case with the reaction of phenol and 2,5-xylenol under equal conditions (over H-MOR-90, figures 5-16 and 5-35, and, over the other catalysts tested figures 5-15, 5-17, 5-34 and 5-36) conversion decreases with increasing space velocity. Unfortunately data from the highest space velocity applied in this experiment is rather scattering.

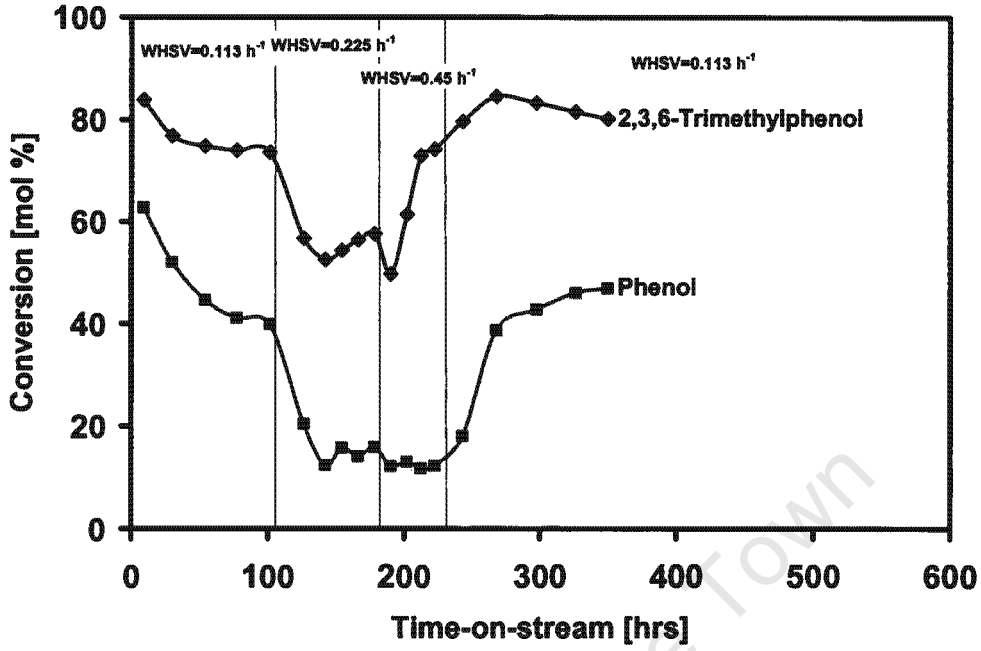


Figure 5-50 (Experiment 6): Conversion versus time-on-stream over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol : 2,3,6-trimethylphenol at a temperature of 350°C

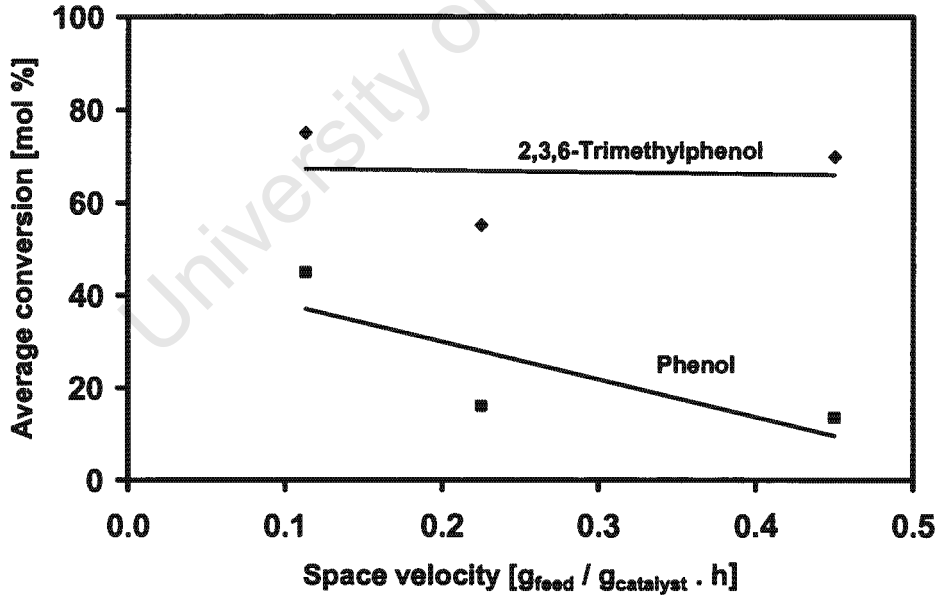


Figure 5-51 (Experiment 6): Average phenol and 2,3,6-trimethylphenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol : 2,3,6-trimethylphenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

Selectivities and yields vary analogously to those obtained from conversion of the phenol / 2,5-xylenol mixtures when varying space velocity. Figure 5-52 shows that the selectivity for other trimethylphenol isomers decreases with increasing 2,3,6-trimethylphenol conversion while the selectivities for all other product fractions increase with increasing 2,3,6-trimethylphenol conversion. Note that xylenols do appear as a new product fraction.

Figure 5-53 shows that the yields for all product fractions, including the other trimethylphenols, increase with increasing 2,3,6-trimethylphenol conversion. Compared at 70 mol % 2,3,6-trimethylphenol conversion, other trimethylphenol isomers are the major product fraction.

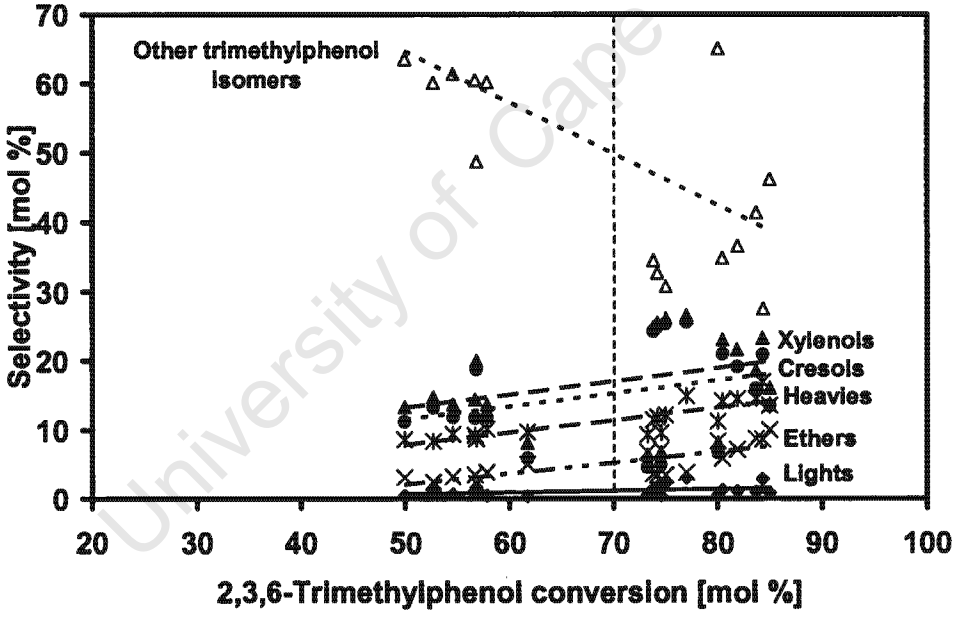


Figure 5-52 (Experiment 6): Selectivity versus 2,3,6-trimethylphenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol : 2,3,6-trimethylphenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

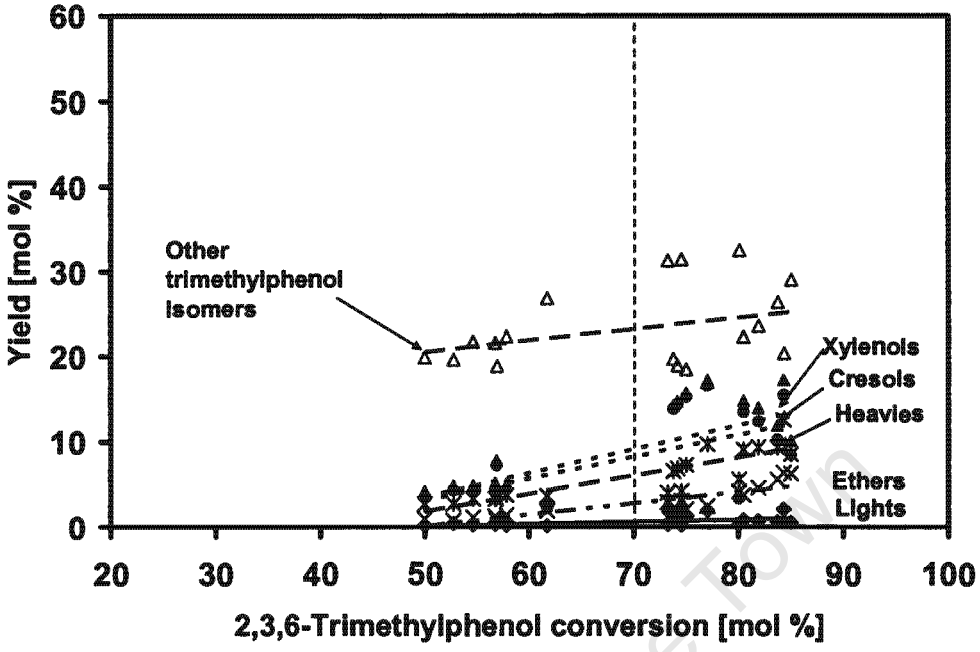


Figure 5-53 (Experiment 6): Yield versus 2,3,6-trimethylphenol conversion over H-MOR-90 catalyst for a 1 : 1 molar ratio feed mixture of phenol : 2,3,6-trimethylphenol at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

5.7.2 Reaction of phenol with the simulated technical mixture

A simulated technical phenolics mixture was produced by alkylating 2,5-xylenol and 2,3,6-trimethylphenol with methanol and flashing most of the low boiling fractions (see section 4.4). This resulted in a product mixture containing a range of higher methylphenols, mainly trimethylphenols (ca. 43 mol %) and tetramethylphenols (ca. 16 mol %) and most probably also pentamethylphenol (as part of 'others'), see table 5-2, middle column. Phenol was added to this simulated technical mixture so that a feed with a ca. 20 : 1 molar ratio resulted for transalkylation studies, see table 5-2, right column. This mixed feed was converted in liquid phase at 60 bar at a temperature of 350°C over H-BEA-25 catalyst at different space velocities.

The composition of the transalkylation product obtained is shown in table 5-3. Tables 5-2 and 5-3, in comparison, show that the amount of cresols and xylenols in the reactor effluent at the lowest space velocity applied (0.11 g_{feed} / $g_{catalyst}$. h) increased from 0.47 to 9.85 mol % and from 0.85 to 2.39 mol %, respectively, while the contents of trimethylphenols and tetramethylphenols have decreased from 2.51 to 1.05 mol % and from 0.94 to 0.08 mol %, respectively. Table 5-4 compares what was consumed and what was gained during the reaction of the mixture. It should be noted that between half and two thirds of the consumed phenol goes into formation of diphenylethers (see table 5-4).

Figures 5-54 to 5-56 show the effect of space velocity on conversion, selectivities and yields.

Table 5-2: Composition of the simulated technical mixture as it was produced (ignoring phenol) and of the feed mixture that was transalkylated, including the added phenol

Component	***Composition (mol %) of simulated technical mixture***	
	Excluding phenol	***Including phenol (ca. 20 : 1, molar)***
Lights	2.16	0.13
Phenol	-	94.17
Cresols	8.07	0.47
Xylenols	14.52	0.85
Trimethylphenols	43.04	2.51
Tetramethylphenols	16.15	0.94
Others	16.06	0.93
Total	**100**	**100**

Table 5-3: Composition of the reactor effluent obtained from reacting the ca. 20 : 1 molar mixture of phenol and simulated technical mixture (table 5-2) over H-BEA-25 zeolite at a temperature of 350°C

Component	*Weight hourly space velocity* (g_{feed} / $g_{catalyst}$. h)		
	0.11	**0.23**	**0.45**
	Composition [mol %]		
Lights	1.88	0.44	0.22
Phenol	52.41	73.61	84.43
Cresols	10.13	5.16	2.72
Xylenols	2.74	2.62	2.25
Trimethylphenols	1.30	0.93	1.27
Tetramethylphenols	0.08	0.14	0.30
Diphenylether*	17.18	11.91	6.09
Phenoxytoluenes*	2.80	0.72	0.31
Others	11.47	4.49	2.40
Total	**100**	**100**	**100**

*Considered as representing two molecules of phenol or alkylphenol (ring balance)

$$2\ phenol \rightarrow 1\ diphenylether + water$$

Table 5-4: Gain/loss of individual compounds and compound fractions through reacting the ca. 20 : 1 molar mixture of phenol and simulated technical mixture over H-BEA-25 zeolite at a temperature of 350°C (difference of table 5-3 and table 5-2 last column data)

Component	*Weight hourly space velocity* (g_{feed} / $g_{catalyst}$. h)		
	0.11	**0.23**	**0.45**
	Differences [mol %]		
Lights	+1.75	+0.31	+0.09
Phenol	-41.76	-20.56	-9.74
Cresols	+9.66	+4.69	+2.25
Xylenols	+1.89	+1.77	+1.40
Trimethylphenols	-1.21	-1.58	-1.24
Tetramethylphenols	-0.86	-0.80	-0.64
Diphenylether*	+17.18	+11.91	+6.09
Phenoxytoluenes*	+2.80	+0.72	+0.31
Others	+10.54	+3.56	+1.47
Total	**-0.01**	**0.00**	**-0.01**

* Considered as representing two molecules of phenol or alkylphenol (ring balance)

2 *phenol* → 1 *diphenylether* + *water*

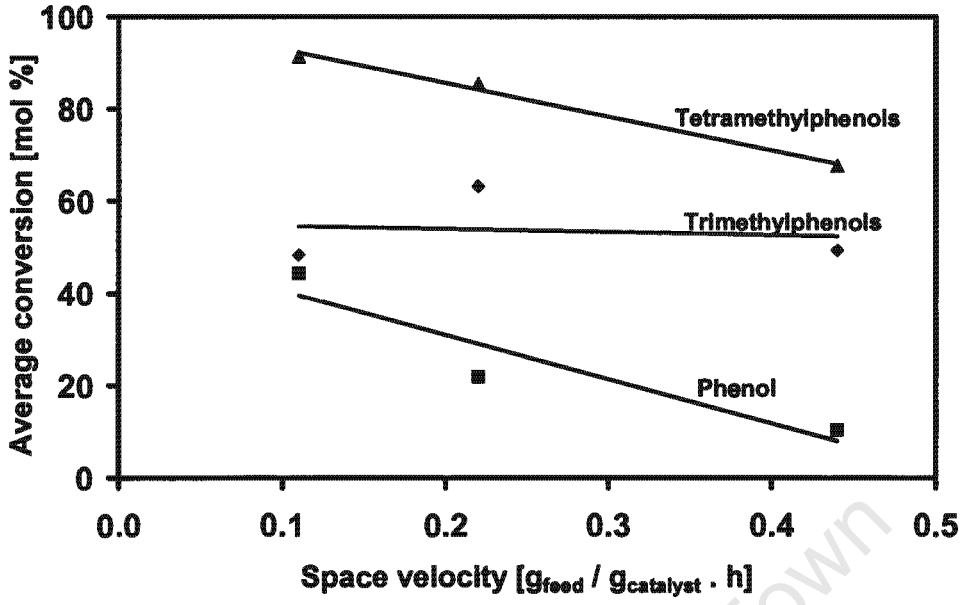


Figure 5-54 (Experiment 9): Average conversions versus space velocity over H-BEA-25 catalyst for the 20 : 1 molar ratio feed mixture of phenol and simulated technical mixture (see table 5-2) at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

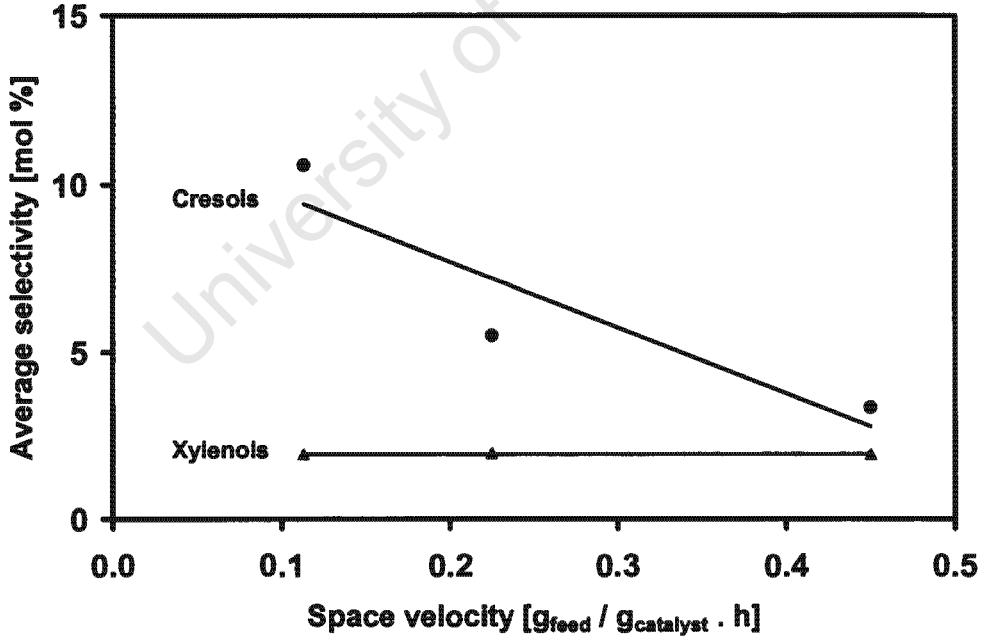


Figure 5-55 (Experiment 9): Average selectivities versus space velocity over H-BEA-25 catalyst for the 20 : 1 molar ratio feed mixture of phenol and simulated technical mixture (see table 5-2) at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

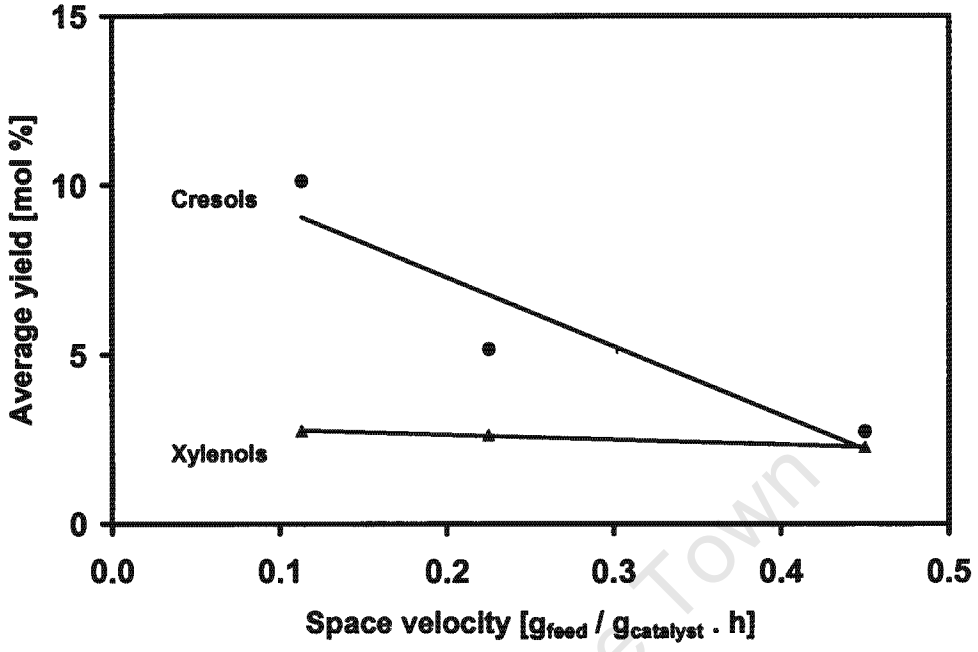


Figure 5-56 (Experiment 9): Average yields versus space velocity over H-BEA-25 catalyst for the 20 : 1 molar ratio feed mixture of phenol and simulated technical mixture (see table 5-2) at a temperature of 350°C and varying space velocities between WHSV = 0.113 h^{-1} and 0.45 h^{-1}

Figure 5-54 shows that conversions of trimethylphenols and tetramethylphenols are rather high, around 55 and 70 mol % respectively, decreasing with increasing space velocity. With phenol, conversion is lower but decreasing steeper, comparatively. Figures 5-55 and 5-56 show that yield of and selectivity towards xylenols are more or less constant with changing space velocity, while yield and selectivity for cresols declines significantly with increasing space velocity.

5.8 Distribution of xylenol isomers from isomerising highly diluted 2,5-xylenol

Figure 5-57 shows the experimentally determined xylenol isomers distribution at 350°C. Note that the mixture has completely reacted through, since changing space velocity to a quarter did not result in any substantial changes anymore .

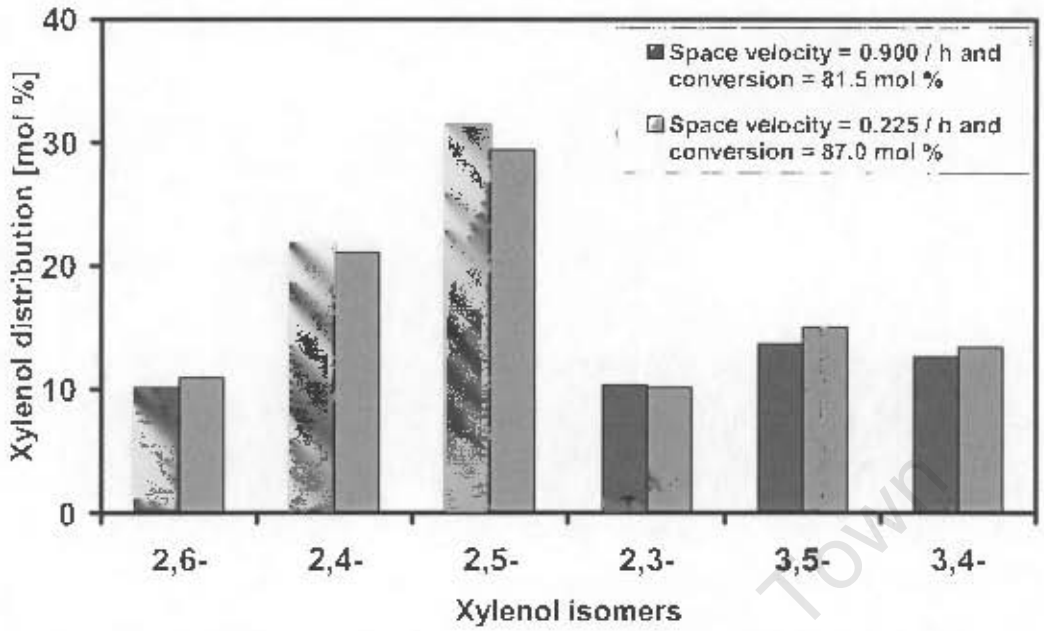


Figure 5-57 (Experiment 11): Experimentally determined distribution of the xylenol isomers from reacting a highly diluted 2,5-xylenol feed over H-BEA-25 catalyst at 350°C and space velocities varying between of 0.225 and 0.900 h^{-1}

Note that the reaction was carried out with inert solvent, benzene, and the resulting distribution only comprises 1,2-methyl shift isomerisation reactions and is not influenced by additional, may be selective, dealkylation reactions.

Chapter 6

DISCUSSION

In this chapter, the results obtained in the transalkylation of phenol with 2,5-xylenol, phenol with 2,3,6-trimethylphenol and phenol with a simulated technical mixture of phenolic compounds over zeolites H-BEA-25, H-MOR-25 and H-MFI-90 are discussed.

6.1 Occurrence of the transalkylation reaction and choice of suitable standard operating conditions.

At 60 bar in liquid phase and space velocities ($WHSV_{total\ feed}$) < 0.5 h^{-1}, a temperature of 350°C was found to be optimum for the transalkylation reaction of phenol with 2,5-xylenol, 2,3,6-trimethylphenol and the simulated technical mixture. This was achieved by carrying out experiments with a phenol / 2,5-xylenol feed mixture over H-BEA-25 catalyst in the temperature range of 250 – 450°C (see section 4.2.1). These experiments also served to test whether transalkylation between phenolic compounds over an acid zeolite catalyst takes place to a sufficient extent.

Figures 4-6, 5-4 and 5-5 show that transalkylation was achieved. This is evident from the formation of cresols, which would result from transfer of a methyl group from a 2,5-xylenol molecule to a molecule of phenol and the formation of trimethylphenols which would result from methyl group transfer between xylenol molecules.

In reacting systems the rate of reaction coefficient (reaction rate constant) is usually a strong function of temperature i.e. the rate of reaction increases with increasing temperature [Schmidt, 2005]. Hence, as expected, results presented

in figures 5-1 to 5-3 show that the conversion of both reactants, phenol and 2,5-xylenol, increased with increasing temperature from 250°C onwards but appeared to level out at around 350°C. Beyond 400°C the conversion of both phenol and 2,5-xylenol declined significantly. Selectivity and yield of the desired product, cresol, also did peak in the 350 – 400°C range, with less "heavies" produced at 350°C (figures 5-4 and 5-5). As a consequence, a temperature of 350°C was chosen for further experiments as mentioned before. A detailed discussion of the temperature effects is given in section 6.4.3, including all temperature variation experiments.

6.2 Catalyst stability and repeatability of experiments

Catalysts were found to exhibit rather fast deactivation during the first ca. 100 hours of operation, though the total initial loss of activity was moderate, after which better stability was achieved for the next more than 100 hours on stream (figures 5-6, 5-7 and 5-12) and sections 5.2 and 5.3.1. Such behaviour is typical for most heterogeneous catalysts, in particular acid zeolites. Consequently, data obtained during the initial period was ignored.

Repeatability in experiments was determined by comparing the conversions of both phenol and 2,5-xylenol at a certain condition with the conversions obtained at the same condition repeated within the same experiment. It was found (see section 5.2) that the conversions at the repeated conditions settings were similar but slightly lower than the conversions at the earlier conditions settings (figures 5-8 and 5-9). Repeatability was also confirmed by results presented in section 5.3.1 and in figures 5-10 and 5-11, where the selectivity is the determining factor.

The repeatability of two identical experiments, done separately, was studied by comparing the conversions of both phenol and 2,5-xylenol and the selectivities obtained from two separate, identical experiments (section 5.3.2 and figures 5-12 to 5-14). Closely matching conversion and selectivity data from the two

experiments gave an indication of good repeatability between experiments and it was therefore concluded that experiments are repeatable. As described in section 5.3.2 (figures 5-12 to 5-14) it is mainly changes during the initial period of runs that causes the moderate differences in conversion and selectivies when repeating conditions, with in particular the selectivity of "heavies" being initially rather high and then settling. It was therefore concluded that experiments were repeatable within the same run provided the very initial data (ca. < 100 hours on stream) was ignored and only the very last data points of the initial conditions setting considered for calculating averages etc. It could also be concluded that, when ignoring short time-on-stream data, results and trends obtained are comparable and valid when varying conditions within a single run.

6.3 Choosing the most suitable catalyst for transalkytion

Screening experiments were carried out with three commercially available candidate catalysts with the objective of choosing the most suitable for the alkylation reaction of phenol with the transalkylating agents 2,5-xylenol, 2,3,6-trimethylphenol and the simulated technical mixture of phenolic compounds. As mentioned in section 5.4, the three catalysts, H-BEA-25, H-MFI-90 and H-MOR-90, were compared in terms of conversion, stability, yield and selectivity.

Figures 5-15 to 5-17 (on the y-axes) and 5-18 to 5-23 (on the x-axes) show that similar phenol and 2,5-xylenol conversions were obtained on zeolites H-BEA-25 and H-MFI-90 at all space velocities applied but higher than on H-MOR-90.

Since H-MFI-90 and H-MOR-90 had the same and rather high molar SiO_2 / Al_2O_3 ratio of 90, these two catalysts were expected to have more or less the same number and strength of Brønsted acid sites and hence similar activities [Martens et al., 1997], see section 2.10.3. However, experimental results showed that H-MFI-90 was more active than H-MOR-90 at all space velocities applied. A

possible reason behind this could be the fact that for large molecules such as the feed molecules H-MOR-90 is effectively one dimensional while H-MFI-90 is three dimensional (see sections 2.12.3 and 2.12.2, respectively). This means, even though H-MOR-90 has larger pores than H-MFI-90, that it is apparently easier for the reactants to enter and the products to leave the channel systems in H-MFI-90 than in H-MOR-90 zeolite crystals. Besides showing the lowest phenol and 2,5-xylenol conversions, zeolite H-MOR-90 also exhibited faster deactivation and apparently no stabilisation after the initial period of the run, which can also be ascribed to the effect of the effectively mono-dimensional pore system (figure 5-16).

Zeolite H-BEA-25 was expected to have more acid sites than H-MFI-90 because of its lower SiO_2 / Al_2O_3 ratio of 25 and was therefore expected to be the more active catalyst. However, though activities of the two for the conversion of the 2,5-xylenol seemed rather equal, this did not hold for the phenol (see figures 5-15 and 5-17). This difference was also reflected in selectivities and yields (figures 5-18, 5-20, 5-21 and 5-23) where the H-MFI-90's product was mainly xylenol isomers, also much heavies, while the H-BEA-25's product consisted for the most of the desired product, cresols. Limited pore system spaciousness, i.e. restricted transition state selectivity, hindering the bulky transalkylation transition states in H-MFI-90, could be a reason why H-MFI-90 showed significantly lower phenol conversion and cresol selectivity (= transalkylation activity) than H-BEA-25.

It was concluded that zeolite H-BEA-25 is the most suitable catalyst for the alkylation reaction of phenol with the transalkylating agents 2,5-xylenol, 2,3,6-trimethylphenol and the simulated technical mixture.

6.4 2,5-Xylenol conversion mechanism

The mechanism shown in figure 6-1 is proposed for the conversion of 2,5-xylenol.

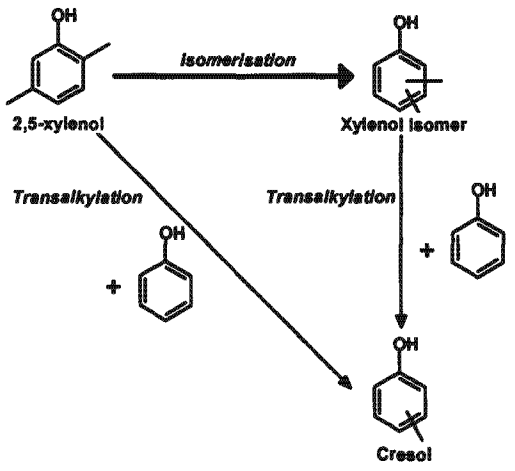


Figure 6-1: The proposed reaction scheme for 2,5-xylenol transformation

At 1 : 1 molar feed ratio of 2,5-xylenol and phenol, 2,5-xylenol conversion is always significantly higher than phenol conversion (see figures 5-1 to 5-3 and 5-15 to 5-17). This holds throughout all of the different conditions applied (figures 5-24 – 5-27, 5-34 – 5-36, 5-43 and 5-44). This is due to the fact that 2,5-xylenol is transformed through two mechanisms namely isomerisation and transalkylation while phenol is only transformed through transalkylation. At low 2,5-xylenol conversion, selectivity of other xylenol isomers (other than the 2,5-isomer) is already high and that of cresols is still low, except for the very high phenol : 2,5-xylenol ratio of 20 : 1 (see figures 5-18 to 5-20, 5-28 – 5-30 and 5-37 – 5-39). This illustrates the fact that isomerisation is fast and thus the preferred step of 2,5-xylenol conversion (the thick arrow in figure 6-1).

At conversions above 50%, yield of cresols still increases (see figures 5-21 to 5-23, 5-31 – 5-33, 5-40 – 5-42 and 5-46) while the yield of other xylenol isomers already declines. Apparently all isomers can and do react in transalkylation i.e. they do not form initially and then go back to 2,5-xylenol through back-isomerisation. This is proven by the percentage of 2,5-xylenol in the xylenols fraction, which is always greater than the equilibrium percentage (figure 6-2).

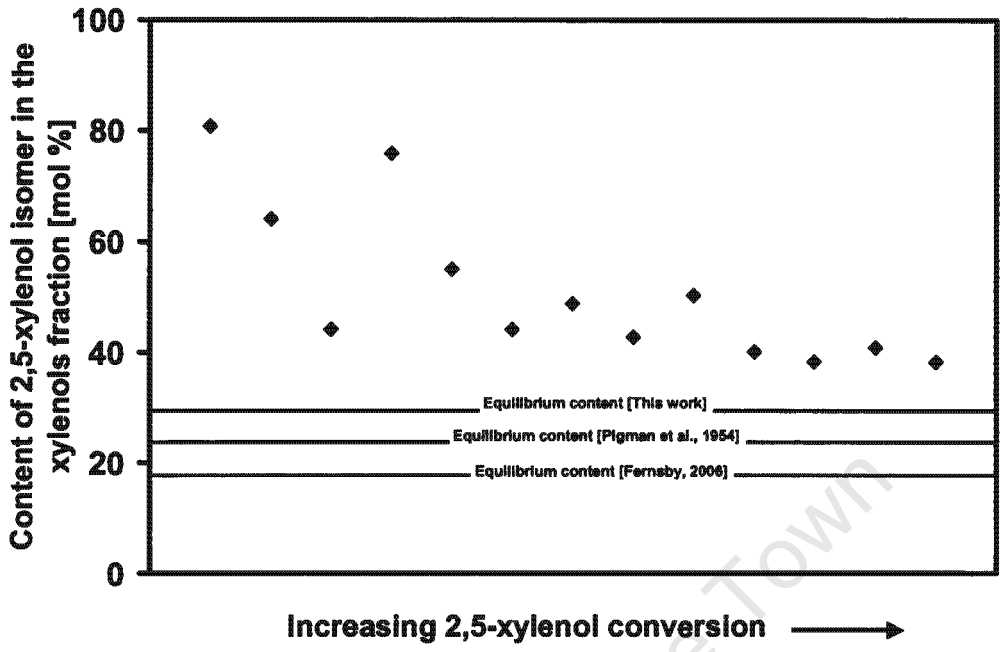


Figure 6-2 (Experiment 1 – 3 and 7 – 8): Content of 2,5-xylenol in the xylenol fractions from reaction over H-BEA-25 at different temperatures, different phenol : 2,5-xylenol feed ratios and different space velocities, see section 2.7.2 for thermodynamic equilibrium distributions measured and calculated by Pigman et al. [1954] and Fernsby [2006], respectively, and section 5.8 for measurements in context of this work

6.5 Isomerisation reaction scheme

The reaction scheme given in figure 6-3 can be proposed for the isomerisation of 2,5-xylenol. It is simply based on the assumption that methyl substituent isomerisation mainly occurs via 1,2-methyl shift, particularly at low to medium conversions, since transalkylation products (yield and selectivity) are still low while isomerisation readily occurs (figures 5-18 – 5-20, 5-28 – 5-33 and 5-37 – 5-42).

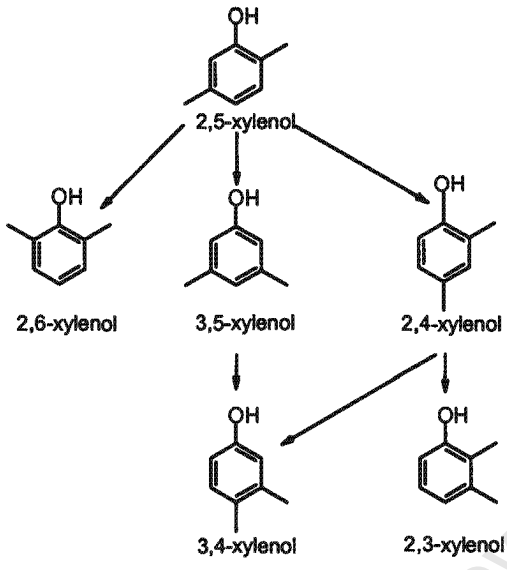


Figure 6-3: Proposed reaction scheme for the isomerisation of 2,5-xylenol by 1,2-methyl shift

According to this mechanism, three isomerisation products form primarily and in parallel, namely 2,6-, 3,5- and 2,4-xylenol, followed by formation of two secondary isomerisation products, 3,4- and 2,3-xylenol. Isomer distributions at low to moderate conversion were expected to reflect the scheme given in figure 6-3.

6.6 Cresol formation reaction scheme

From the transalkylation reaction of phenol and 2,5-xylenol, applying simple statistical bond cleavage and formation rules, either o-cresol and a second cresol molecule or m-cresol and a second cresol molecule would form and the second cresol molecule could be o-, p- or m-cresol (figure 6-4) with o- : m- : p-cresol distribution in 45 : 45 : 10 percent ratio.

Applying basic chemical kinetic rules, i.e., the m-position being non-reactive, would also form each of the isomers (figure 6-5), with o- : m- : p-cresol in 33 : 50 : 17 percent ratio.

Unfortunately, there is not much of a difference between these theoretical cresol distributions and the thermodynamic equilibrium distribution, see table 6-1, in particular of the latter, chemically controlled distribution. In section 6.9, cresol formation and selectivity are discussed in more detail.

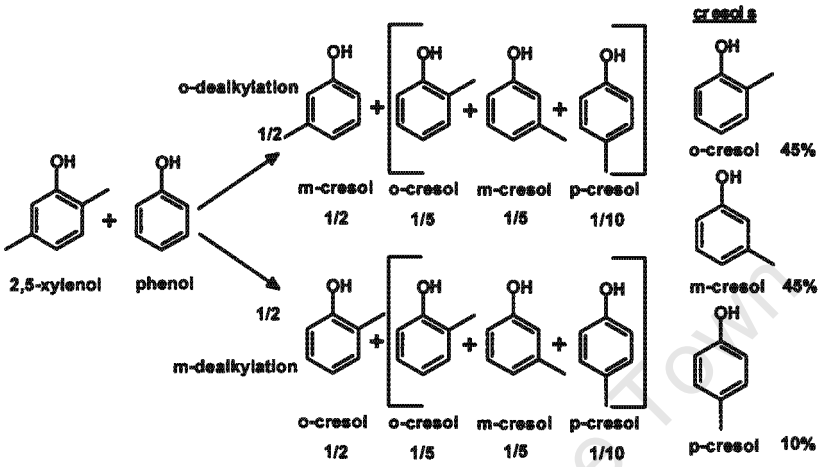


Figure 6-4: Possible reaction scheme for the formation of cresols from the transalkylation reaction of 2,5-xylenol and phenol applying statistical rules

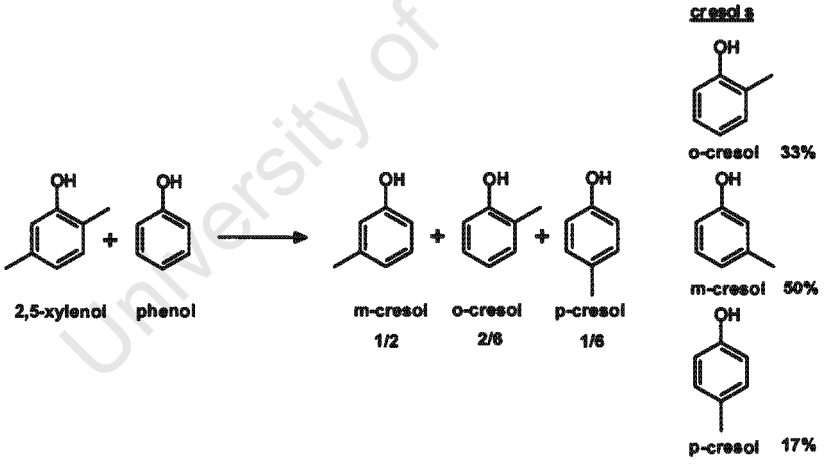


Figure 6-5: Possible reaction scheme for the formation of cresols from the transalkylation reaction of 2,5-xylenol and phenol applying basic chemical rules

The cresol selectivity at lowest conversion can be assumed to be closest to the primary product of phenol and 2,5-xylenol transmethylation i.e. there is less product from other xylenol isomers and less product from secondary isomerisation of the initially formed cresols.

6.7 Effect of reaction conditions

6.7.1 Effect of phenol : 2,5-xylenol ratio

Conversion of phenol and 2,5-xylenol was found to decrease with increasing phenol : 2,5-xylenol ratio (figures 5-26 and 5-27). The relative decrease of the conversion of phenol with increasing feed ratio (figure 5-26) is more significant, simply due to the corresponding increase in the total mol fraction of phenol in the feed mixture, but there is little decrease only in 2,5-xylenol conversion. Indeed the conversion of 2,5-xylenol was not expected to decrease with increasing phenol : 2,5-xylenol ratio. A change of the feed ratio would result in the mol fraction of 2,5-xylenol being changed compared to its former level. However, when assuming a first order reaction for isomerisation, this should not affect isomerisation conversion at all as long as transalkylation does not consume substantially (in consecutive reaction steps) from the isomers formed (see figure 6-1), i.e. as long as yields of transalkylation and other products are low. As shown in figures 5-23, 5-31 and 5-32, this does not hold anymore for the low feed ratios, what may cause the slight decrease in isomers yield with the decline in feed ratios in figure 6-6.

When assuming a second order transalkylation reaction of 2,5-xylenol with phenol, which is of first order in each of the reactants, the rate of the transalkylation reaction would be reduced to just about half in the 5 : 1 molar mixture and to about 1/5 in the 20 : 1 mixture, while the mol fractions of xylenols in the feed would be reduced by 1/3 and about 1/10 respectively (Appendix C). This should even result in a slight increase in the transalkylation conversion of 2,5-xylenol in the 5 : 1 mixture and for the 20 : 1 ratio experiment. The increase in conversion of 2,5-xylenol in the transalkylation reaction should be almost twice (Appendix C), which is clearly not the case, even when not considering the 'other reactions' (figure 6-6). Apparently in liquid phase the transalkylation reaction is closer to first order, than second order.

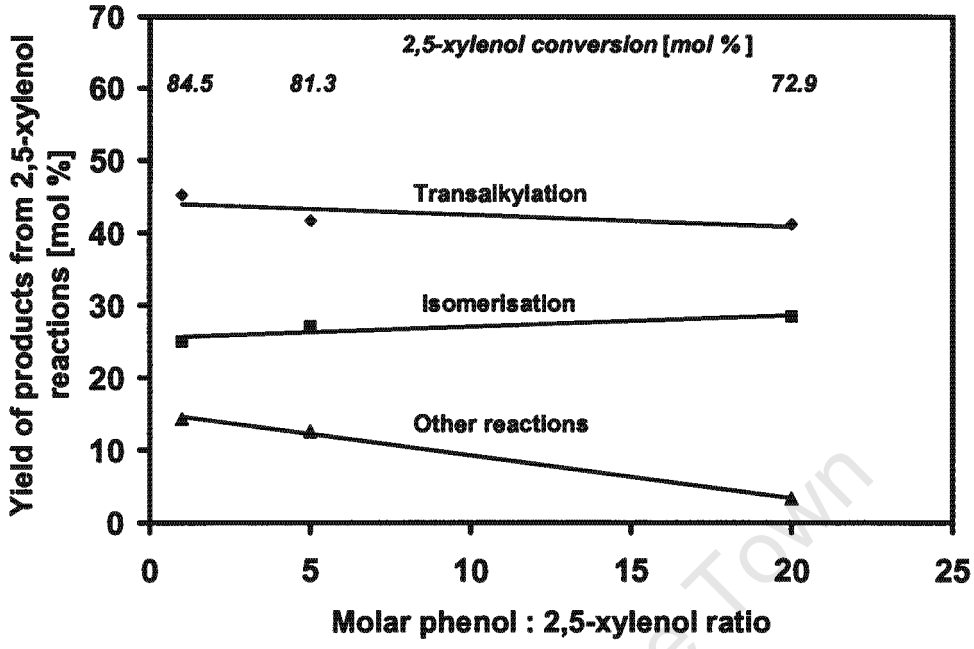


Figure 6-6 (Experiments 3, 7 and 8): Direction of 2,5-xylenol transformation versus the molar ratio of the feed mixture of phenol and 2,5-xylenol over H-BEA-25 at a temperature of 350°C and space velocity of 0.113 h^{-1}. Note that transalkylation yield refers only to the 2,5-xylenol molecules that have reacted

The evaluation of transalkylation, isomerisation and other reactions in figure 6-6 was based on the following equations.

Isomerisation = *Yield of all xylenol isomers excluding 2,5-xylenol*

Transalkylation = *Sum of yields of (i) cresols from transalkylation of phenol with 2,5-xylenol and (ii) cresols and trimethylphenols from disproportionation of 2,5-xylenol*

With:

(i) $Yield_{Cresols\ from\ transalkylation} = Yield_{Cresols} - Yield_{Cresols\ from\ disproportionation} = Yield_{Cresols} - Yield_{Trimethylphenols}$ (Since $Yield_{Cresols\ from\ disproportionation} = Yield_{Trimethylphenols}$)

Must be divided by 2 since half of the rings is coming from phenol

$$(ii)\,Y_{Cresols\ and\ trimethylphenols\ from\ disproportionation} = 2\,Yield_{Trimethylphenols}$$

$$\therefore Transalkylation = \frac{Yield_{Cresols} - Yield_{Trimethylphenols}}{2} + 2Y_{Trimethylphenol}$$

$$\Rightarrow Transalkylation = \frac{Yield_{Cresols}}{2} + 2\,Yield_{Trimethylphenols} - \frac{Yield_{Trimethylphenols}}{2}$$

$$\Rightarrow Transalkylation = \frac{Yield_{Cresols}}{2} + \frac{2(2Yield_{Trimethylphenols})}{2} - \frac{Yield_{Trimethylphenols}}{2}$$

$$\Rightarrow Transalkylation = \frac{Yield_{Cresols}}{2} + \frac{3Yield_{Trimethylphenols}}{2}$$

$$Other\ reactions = 2,5\text{-}xylenol\ consumed - Isomerisation - Transalkylation$$

It should be noted that these quantities were normalised to a 100 to convert them to selectivities as presented in figure 6-6.

A steep increase in the selectivity for ethers with increasing phenol : 2,5-xylenol ratio was obtained (figures 5-20 and 5-28 – 5-30). Increased selectivity towards ethers was expected because the increasing phenol concentration with increasing ratio results in an increased chance of an adsorbed phenol molecule to be approached by another phenol molecule and the only way for the two reacting with each other is the formation of diphenylether, which is indeed the most abundant of the ethers obtained. While yields of all product fractions were found to decrease with increasing phenol : 2,5-xylenol ratio (infact trivial, since all other products require 2,5-xylenol being involved, whose concentration in the feed mixture declines), the yield of ethers was found to be more or less constant (figure 5-33) and eventually dominating the product (figure 5-30). Since each of the compounds in the feed mixture is phenolic, the concentration of OH-groups and thus the rate of formation of ethers i.e. the yield of ethers would not be expected to increase or decrease with increasing phenol : 2,5-xylenol ratio.

Selectivity towards trimethylphenols was found to decrease steeply (comparatively) with increasing phenol : 2,5-xylenol ratio. At the highest phenol : 2,5-xylenol molar ratio of 20 : 1, the selectivity towards trimethylphenols was found to be virtually zero. This happens because, trimethylphenols would primarily result from a disproportionation of 2,5-xylenol or other xylenol isomers and if fewer xylenol molecules are present, it means that the chances of the bimolecular, i.e. second order disproportionation reaction of xylenols taking place are very small, hence much less of the trimethylphenols will form.

Tiwari and Mukherjee [1984] also noticed a decrease in the formation of trimethylphenols and isomerisation products (xylenol isomers) when they were experimenting with mixtures with increasing ratios of phenol : 2,6-xylenol over a chromia-alumina catalyst. This was attributed to, analogously, the fact that at high phenol : 2,6-xylenol ratios, the catalyst surface is extensively covered by phenol, so that a released methyl group has hardly any chance of reacting with a xylenol molecule.

The constant selectivities for lights and heavies (figure 5-30) but declining yields (figure 5-33) indicate towards a complex mechanistic pathway, which may not be understood since the mechanism of their formation (lights) and the exact nature of the heavies is unidentified.

6.7.1.1 Effect of phenol : 2,5-xylenol molar ratio on the cresols and xylenols distribution

Figure 6-7 shows that at all the phenol : 2,5-xylenol ratios investigated a slightly higher yield of meta-cresol is obtained than that of ortho-cresol and a significantly higher yield of ortho-cresol is produced than para-cresol.

Table 6-1 shows the distribution of the cresol isomers at different phenol : 2,5-xylenol molar ratios. The distributions obtained at both the 1 : 1 and

5 : 1 molar ratios are very close to equilibrium distribution and equilibrium distribution is obtained at a ratio of 20 : 1. However, as discussed in section 6.9, this is in any case still a kinetically controlled cresol isomer distribution, which, by chance, is numerically similar to equilibrium distribution.

Table 6-1 (Experiments 3, 7 and 8): Distribution of the cresol isomers at different phenol : 2,5-xylenol feed ratios over H-BEA-25 at a temperature of 350°C, space velocity of 0.113 h^{-1} and distribution in thermodynamic equilibrium

2,5-Xylenol Conversion (mol %)	*Molar phenol : 2,5-xylenol ratio*			**Equilibrium Distribution at 380°C*
	1:1	5:1	20:1	
	84.5	79.7	70.9	
Compound	*Amount (mol %)*			
o-Cresol	38.2	39.1	36.8	36
p-Cresol	17.3	17.3	15.8	16
m-Cresol	44.5	43.6	47.4	48

* [Imbert et al., 1997, in gas phase and Fritsch et al., 2003, in liquid phase]

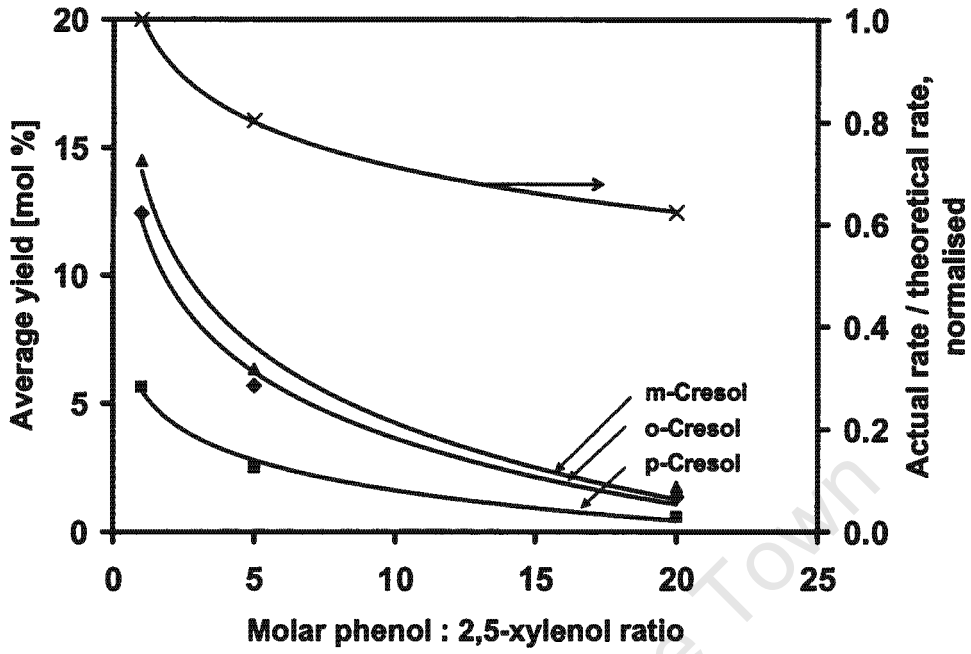


Figure 6-7 (Experiments 3, 7 and 8): Average yields of cresol isomers (left axis) versus the molar phenol to 2,5-xylenol ratio in feed mixtures over H-BEA-25 at a temperature of 350°C and space velocity of 0.113 h^{-1}. This graph also compares the actual and theoretical rates of cresols formation (right axis) versus the ratio

Figure 6-7 also shows that the actual rate (experimental) of cresol formation is declining relative to the theoretical rate over increasing phenol : 2,5-xylenol ratios in the feed, with the theoretical rate assuming first order in each of the reactants in the bimolecular transalkylation between 2,5-xylenol and phenol. This is shown by the declining uppermost curve, X-shaped symbols, in figure 6-7. See also corresponding discussion in section 6.7.1.

The declining rate with increasing phenol : 2,5-xylenol ratio is probably (in part) due to decreasing contribution of formation of cresols via 2,5-xylenol disproportionation as a result of decreasing 2,5-xylenol concentration. Decreasing 2,5-xylenol disproportionation rate is confirmed by the decreasing yield of trimethylphenols (co-product of 2,5-xylenol disproportionation) with increasing phenol : 2,5-xylenol ratio (figure 5-33).

Figure 6-8 and table 6-2 show the yields and distributions of the xylenol isomers in the product and in thermodynamic equilibrium. Note that the isomerisation reaction is assumed to be of first order, i.e. independent from concentration, and that, correspondingly, 2,5-xylenol conversions are similar.

At the moment this product distribution cannot be reasonably explained on the basis of thermodynamics or the mechanism shown in figure 6-3. Aspects such as the 2,3- / 2,4-xylenol ratio, with the former being formed from the latter (in the suggested mechanism, figure 6-3) but present at far higher than equilibrium ratios (see table 6-2), are unresolved questions.

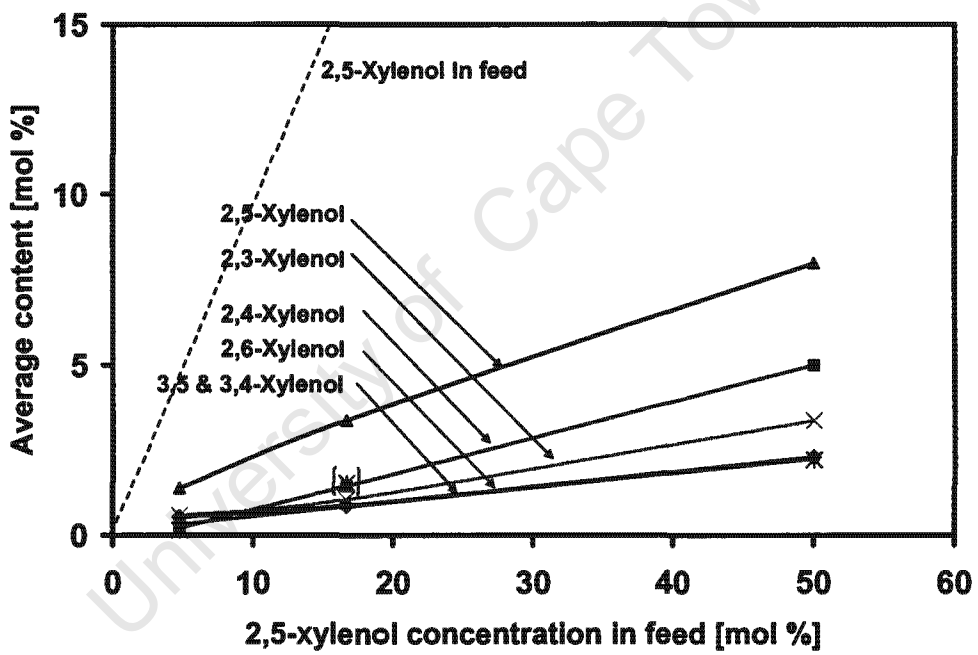


Figure 6-8 (Experiments 3, 7 and 8): Content of xylenol isomers versus 2,5-xylenol concentration of feed over H-BEA-25 at a temperature of 350°C and space velocity of 0.113 h^{-1}

The distribution of xylenol isomers at different phenol : 2,5-xylenol ratios in the feed is shown in table 6-2. It should be noted that the equilibrium distribution of 3,4- and 3,5-xylenols is combined as the peaks of these two isomers were not separated on the gas chromatogram trace.

No conclusion can be made with regard to xylenol isomers approach to equilibrium due to variability in the equilibrium distribution obtained from different sources (table 6-2) and the apparent fact that several isomer ratios (e.g 2,6- / 2,5- and 2,3- / 2,4-xylenol) are exceeding the values that are thermodynamically possible within a scheme of consecutive reactions as suggested in figure 6-3..

Table 6-2 (Experiments 3, 7 and 8): Distribution of the xylenol isomers at different phenol : 2,5-xylenol feed ratios over H-BEA-25 at a temperature of 350°C and a space velocity of 0.113 h^{-1} and distribution in thermodynamic equilibrium

2,5-Xylenol Conversion (mol %)	*Molar phenol : 2,5-xylenol ratio*			*Equilibrium Distribution at 350°C (mol %)*		
	1:1	5:1	20:1			
	84.5	79.7	70.9			
Compound	*Amount (mol %)*			*	**	***
2,6-Xylenol	11.0	10.5	18.6	12.9	11.1	10.9
2,4-Xylenol	23.9	17.5	7.3	43.5	29.6	21.1
2,5-Xylenol	38.2	40.9	48.7	17.7	23.7	29.4
2,3-Xylenol	16.2	12.6	20.4	3.6	8.9	10.2
3,5-Xylenol	10.6****	18.5****	5.0****	16.3	14.1	15.0
3,4-Xylenol				6.1	12.6	13.4

*[Fernsby, 2006]

**[Pigman et al., 1954]

***[This work (figure 5-57)]

****Peaks not separated in GC trace

6.7.1.2 Effect of phenol : 2,5-xylenol ratio on the carbon number distribution

Carbon number distributions for the transalkylation product from different phenol : 2,5-xylenol ratios are given together with the corresponding methyl group balances in figures 6-9 to 6-11 and tables 6-3 to 6-5. For all the phenol : 2,5-xylenol ratios applied, the carbon number distributions obtained seem to approach the calculated equilibrium distribution with decreasing space velocity. The carbon number equilibrium distribution was calculated using a method of minimising the total Gibbs energy of a reaction mixture (appendix D).

Methyl group balances were determined to validate the carbon number distributions obtained experimentally at each phenol : 2,5-xylenol ratio and different space velocities applied. From tables 6-3 to 6-5, it can be seen that for some carbon number distributions the methyl groups do not balance very accurately i.e. the content of methyl groups in the product is not equal to the content in the feed. However, the discrepancy is acceptable and may be attributed to GC analysis.

Given the above mentioned inaccuracies in the methyl group balances, it should not be speculated if the lower-than-equilibrium levels of phenol in figure 6-9 are real or not and about the mechanisms behind it.

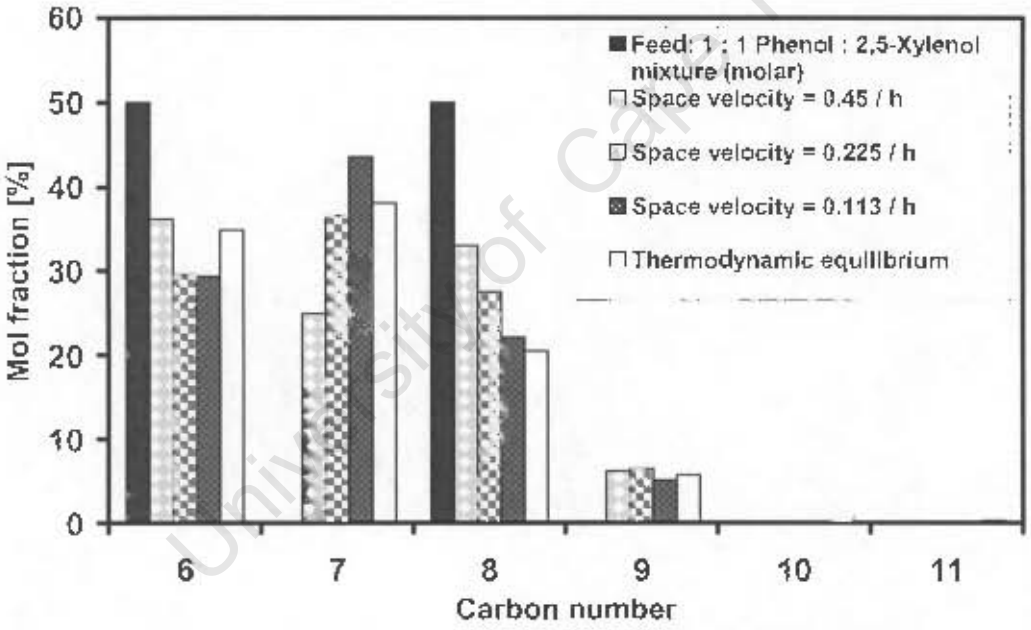


Figure 6-9 (Experiment 3): Carbon number distribution over H-BEA-25 catalyst for a 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol (average carbon number = 7) and transalkylation product at a temperature of 350°C and varying space velocities

The higher the phenol : 2,5-xylenol ratio, the slower is the approach of the reaction mixture to thermodynamic equilibrium distribution. This is not surprising, since the conversion of xylenol must be higher, increasing from about 60% in the 1 : 1 molar ratio feed to about 90% in the 20 : 1 molar ratio feed.

Table 6-3 : Methyl group balance for the carbon number distribution obtained over H-BEA-25 catalyst for 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities and distribution in thermodynamic equilibrium

Carbon number	*Feed*	*Methyl*	*Methyl group out*			
		group in	**Sp=0.11*	**Sp=0.22*	**Sp=0.45*	*Eq.***
6	50.0	0.0	0.0	0.0	0.0	0.0
7			43.6	36.7	24.9	38.2
8	50.0	100.0	44.1	54.9	65.8	40.8
9			15.3	19.4	18.5	17.1
10			0.0	0.0	0.0	2.9
11			0.0	0.0	0.0	1.2
Total		**100.0**	**103.0**	**110.9**	**109.2**	**100.2**

*Space velocity (WHSV) h^{-1}

**Equilibrium

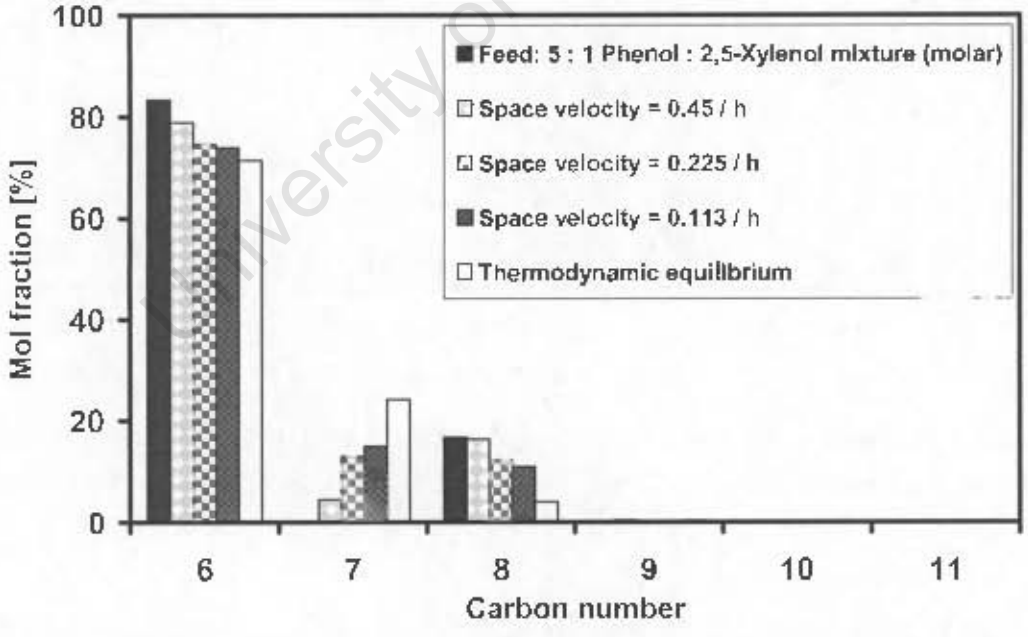


Figure 6-10 (Experiment 7): Carbon number distribution over H-BEA-25 catalyst for a 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol (average carbon number = 6.3) and the transalkylation product at a temperature of 350°C and varying space velocities

Table 6-4 : Methyl group balance for the carbon number distribution obtained over H-BEA-25 catalyst for 5 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities and distribution in thermodynamic equilibrium

Carbon number	*Feed*	*Methyl group in*	*Methyl group out*			
			**Sp=0.11*	**Sp=0.22*	**Sp=0.45*	*Eq.***
6	83.3	0.0	0.0	0.0	0.0	0.0
7			15.0	13.0	4.4	24.2
8	16.7	33.3	21.9	24.3	32.6	8.0
9			0.6	0.9	1.2	1.0
10			0.0	0.0	0.0	0.1
11			0.0	0.0	0.0	0.0
Total		**33.3**	**37.5**	**38.2**	**38.3**	**33.3**

*Space velocity (WHSV) h^{-1}

**Equilibrium

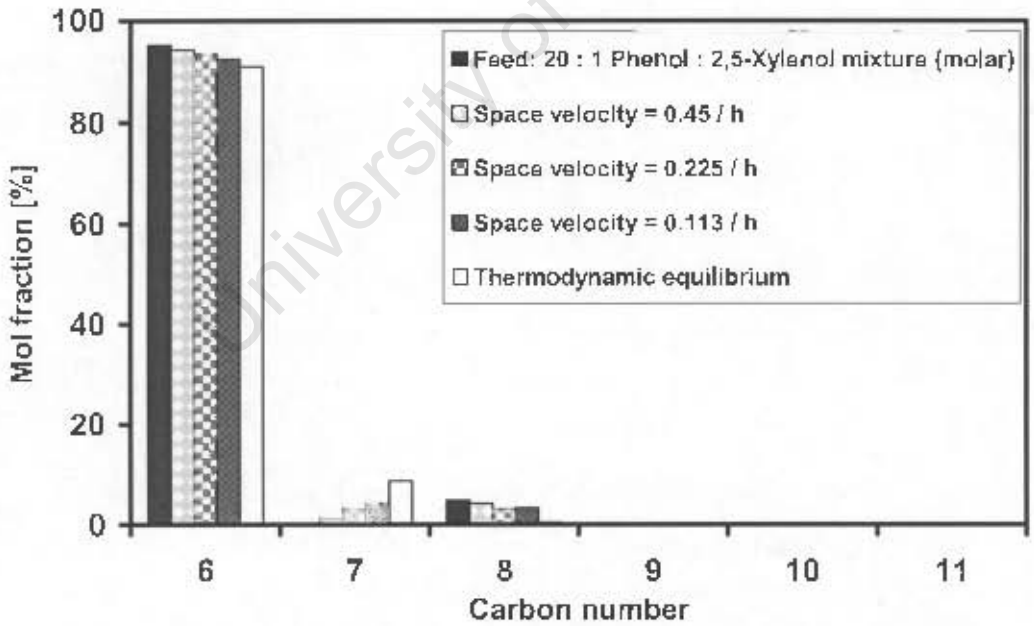


Figure 6-11 (Experiment 8): Carbon number distribution over H-BEA-25 catalyst for a 20 : 1 molar ratio feed mixture of phenol and 2,5-xylenol (average carbon number = 6.1) and the transalkylation product at a temperature of 350°C and varying space velocities

Table 6-5 : Methyl group balance for the carbon number distribution obtained over H-BEA-25 catalyst for 1 : 1 molar ratio feed mixture of phenol and 2,5-xylenol at a temperature of 350°C and varying space velocities

Carbon number	*Feed*	*Methyl group in*	*Methyl group out*			
			**Sp=0.11*	**Sp=0.22*	**Sp=0.45*	*Eq.***
6	95.2	0.0	0.0	0.0	0.0	0.0
7			4.2	3.3	1.4	8.7
8	4.8	9.6	6.6	6.2	8.4	0.8
9			0.6	0.7	0.6	0.0
10			0.0	0.0	0.0	0.0
11			0.0	0.0	0.0	0.0
Total		**9.6**	**11.3**	**10.2**	**10.4**	**9.5**

*Space velocity (WHSV) h^{-1}

**Equilibrium

With increasing phenol : 2,5-xylenol ratio, a shift of the carbon number distribution to lower carbon numbers is seen in figures 6-9 to 6-11. This was expected given the declining average carbon number of the feed.

One of the main objectives of this study was to convert polymethylphenols (C_{9+}) to cresols and xylenols (products of lower carbon number). Increasing phenol : 2,5-xylenol molar ratio seems to achieve this. However very small amounts of cresols are obtained from the higher phenol : 2,5-xylenol ratios of 5 : 1 and 20 : 1 compared to the amount obtained from a 1 : 1 ratio (figures 6-9 to 6-11). Even though higher phenol : 2,5-xylenol ratios lower the carbon numbers, it would be costly (considering the heating and cooling costs for phenol recycling) to separate the lower boiling excess phenol from the products of interest. Applying a low molar feed ratio of about 1 : 1 results in comparably small amounts of surplus phenol which would be less costly to separate from the product. At the low phenol : 2,5-xylenol ratio of 1 : 1, relatively large amounts of

cresols are already obtained. Even though considerable amounts of higher phenols still form at low phenol : 2,5-xylenol molar ratios, and also ethers, see figures 5-52 and 5-53, they may be recycled without the necessity of separating them from the unconverted feed. This is because these higher phenols can also still undergo transalkylation with phenol to produce cresols and xylenols, as discussed in section 6.9.1, and ethers will be cleaved or net formation will be suppressed, respectively. This then makes operating at around a 1 : 1 molar ratio the better and promising option for industrial application.

6.7.2 Effect of space velocity

Conversion of phenol and 2,5-xylenol was found to decreases with increasing space velocity (figures 5-34 to 5-36). The effect of increasing space velocity (decreasing residence time) is more pronounced with phenol than with 2,5-xylenol. This is due to the fact that isomerisation is a faster reaction than transalkylation (see section 2.2.5) and thus closer to completion, i.e. thermodynamic equilibrium, than the transalkylation reaction. However, over the most acidic catalyst, H-BEA-25, even phenol conversion and thus the cresol yield, figures 5-36 and 5-42, cannot increase much anymore at the lowest space velocity. It should also be noted that thermodynamic equilibrium limits phenol conversion in transalkylation of a 1 : 1 mixture with 2,5-xylenol to 65% (see figure 6-9), not considering possible side reactions.

Phenol can react in two ways, i.e., it can react with xylenols in a transalkylation reaction or with itself to produce ethers. 2,5-xylenol undergoes similar reactions and in addition it can also undergo isomerisation and transalkylation with 'itself' (disproportionation).

Selectivity and yield of 'other xylenol isomers' were found to decrease with decreasing space velocity (figures 5-37 to 5-42). 'Other xylenol isomers' result from the isomerisation of 2,5-xylenol. The isomerisation reaction, in terms of

activation energy and steric/geometrical requirements [Böhringer, 2006], is an easy and fast reaction which rapidly achieves high conversion and gets close to xylenols equilibrium distribution at high conversions. The more demanding, slower transalkylation reaction, disproportionation to cresols and trimethylphenols, formation of heavies etc., consume not only 2,5-xylenol but also its isomerisation products. Low space velocity allows for more transalkylation to occur which leads to more isomerisation products being consumed and hence a decrease in yield and selectivity of the xylenol isomers with decreasing space velocity (figure 5-40 – 5-42).

Selectivity and yield for all other product fractions except 'other xylenol isomers' increased with decreasing space velocity. Apparently, reactions leading to the formation of all the other products require more severe conditions (longer residence times) due to e.g. higher activation energies, reflecting geometrical needs etc. The slightly decreasing selectivity and yield for trimethylphenols with increasing space velocity over H-BEA-25 zeolite, figures 5-39 and 5-42, is not understood but may just be data scatter (three data points only).

6.7.2.1 Effect of space velocity on the distribution of cresols and xylenols

Figure 6-12 shows that the yield of m-cresol is slightly higher than that of o-cresol and more than twice as high as the yield of p-cresol at low space velocity seemingly indicating towards a close approach to thermodynamic equilibrium distribution (table 6-6). However, it was mentioned above (see section 6-6) and will be discussed in more detail in section 6.9 that the kinetically controlled reactions would result in a similar cresols distribution.

At the low space velocity, total cresol yields are higher than 30%, slowly approaching the thermodynamic limit value of 38% of cresols in the equilibrated carbon number distribution of 1 : 1 molar feed (see figure 6-9).

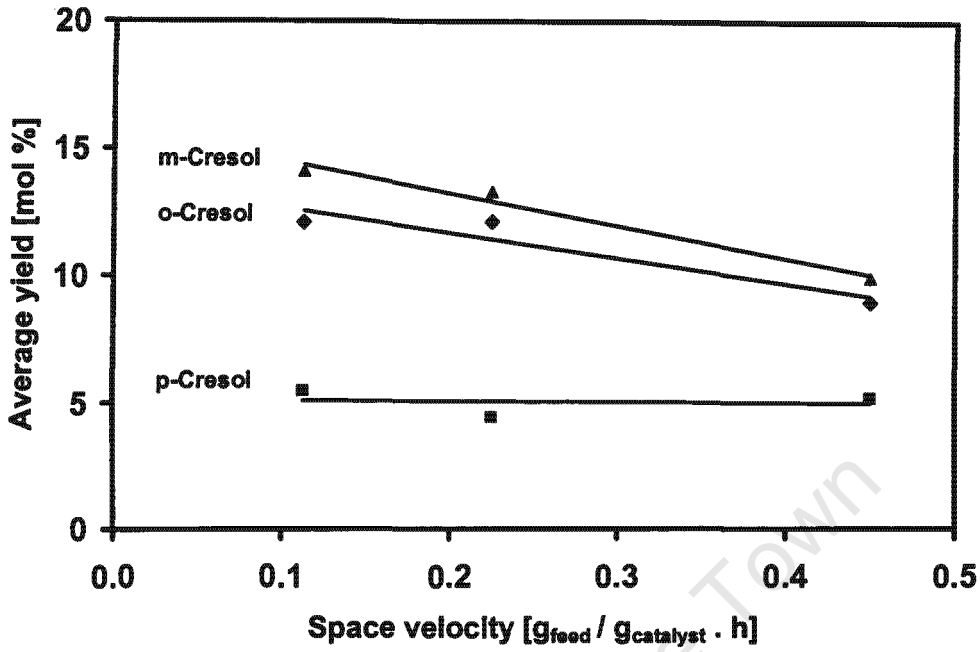


Figure 6-12 (Experiment 3): Average yields of cresol isomers versus space velocity for a phenol : 2,5-xylenol molar feed ratio of 1 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-6 (Experiment 3): Distribution of the cresol isomers at different space velocities for a 1 : 1 molar ratio feed mixture of phenol : 2,5-xylenol over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium

2,5-Xylenol Conversion (mol %)	*Space velocity (WHSV) h^{-1}*			**Equilibrium Distribution at 380°C*
	0.113	**0.225**	**0.45**	
	84.5	85.0	76.5	
Compound	***Amount (mol %)***			
o-Cresol	38.2	40.6	37.2	36
p-Cresol	17.3	14.8	21.5	16
m-Cresol	44.5	44.6	41.2	48

* [Imbert et al., 1997, in gas phase and Fritsch et al., 2003, in liquid phase]

Figure 6-13 shows that, if ignoring 2,5-xylenol (feed component), the highest yields are obtained for 2,4-xylenol at all space velocities. Table 6-7 shows the distribution of the xylenol isomers at different space velocities. Not much can be derived from this figure and table in terms of the effect of space velocity on isomer distribution.

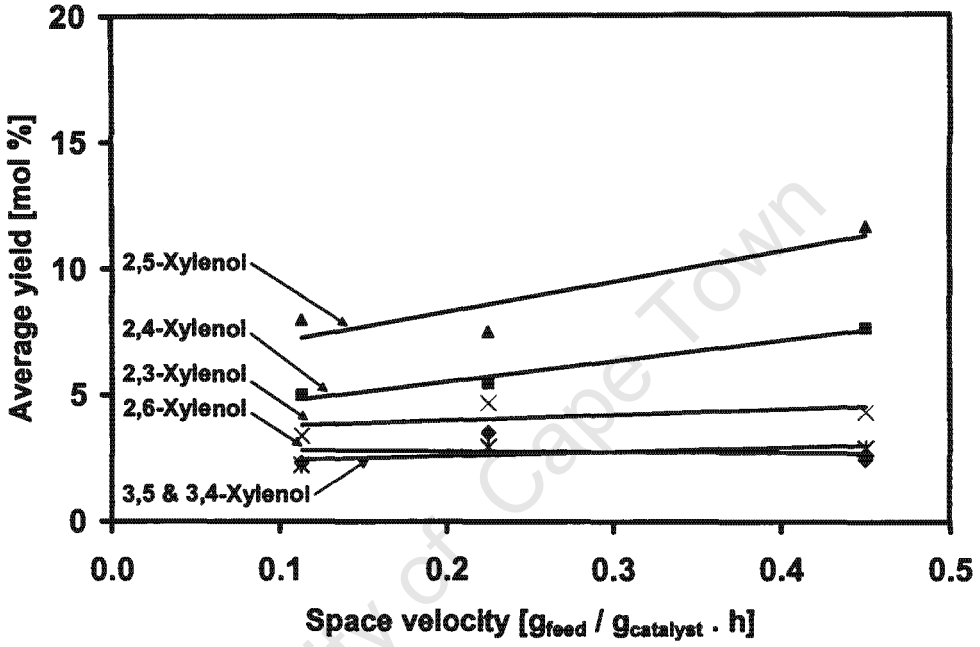


Figure 6-13 (Experiment 3): Average yields of xylenols versus space velocity for a phenol : 2,5-xylenol molar feed ratio of 1 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-7 (Experiment 3): Distribution of the xylenol isomers at different space velocities for a 1 : 1 molar ratio feed mixture of phenol : 2,5-xylenol over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium

2,5-Xylenol Conversion (mol %)	*Space velocity (WHSV) h^{-1}*			*Equilibrium Distribution at 350°C (mol %)*		
	0.113	0.225	0.45			
	84.5	85.0	76.5			
Compound	*Amount (mol %)*			*	**	***
2,6-Xylenol	11.0	14.6	8.5	12.9	11.1	10.9
2,4-Xylenol	23.9	22.7	26.4	43.5	29.6	21.1
2,5-Xylenol	38.2	31.1	40.1	17.7	23.7	29.4
2,3-Xylenol	16.2	19.4	15.0	3.6	8.9	10.2
3,5-Xylenol	10.6****	12.2****	10.1****	16.3	14.1	15.0
3,4-Xylenol				6.1	12.6	13.4

*[Fernsby, 2006]

**[Pigman et al., 1954]

***[This work (figure 5-57)]

****Peaks not separated in GC trace

6.7.3 Effect of temperature

In both temperature series carried out, average conversion, selectivity to cresols and cresol yields were found to increase from 250°C, level out at around 375°C, and decrease rapidly with further increase of temperature (figures 5-3 – 5-5 and 5-44 – 5-46). The rapid decrease with increasing temperature is possibly due to accelerated catalyst deactivation as indicated in all of the curves showing conversion as a function of time-on-stream (figure 5-1, 5-2 and 5-43) in particular at the highest temperature setting of each of the two series (figure 5-2). At 450°C the reaction system may not have been in liquid phase anymore. Unfortunately, no repeat of a lower temperature setting was carried out after running at 450°C, the highest temperature setting of the series. At high temperatures, very high

yields of heavies are achieved (figures 5-5 and 5-46) i.e. the formation of big molecules is accelerated. These big molecules are likely to lead to accelerated coking and plug the pores of the catalyst, this resulting in fast declining catalyst activity.

6.7.3.1 Effect of temperature on the distribution of cresols and xylenols

Figure 6-14 shows that almost equal yields are obtained for m-cresol and o-cresol over a wide temperature range and that a slightly higher yield of m-cresol than o-cresol is only obtained at temperatures of 400 and 450°C. The yield of both m- and o-cresol is about twice as high as that of p-cresol at all temperatures. With meta-cresol being the thermodynamically favoured isomer, this suggests that with increasing temperatures an equilibrium distribution is approached and is confirmed by the cresol isomers distribution given in table 6-8 which shows an approach to equilibrium distribution with increasing temperature.

To quantify the effect of temperature, it would be desirable to determine activation energies, however it makes not much sense in this case. This is because the curves for the three isomers start flattening from 300°C onwards (figure 6-14) and also distributions are close to equilibrium throughout (table 6-8). Though the primary, kinetically controlled product distributions are quite similar (see sections 6.6 and 6.9) it cannot be ruled out that the reaction to the individual isomers is already influenced by thermodynamics and not only governed by kinetics.

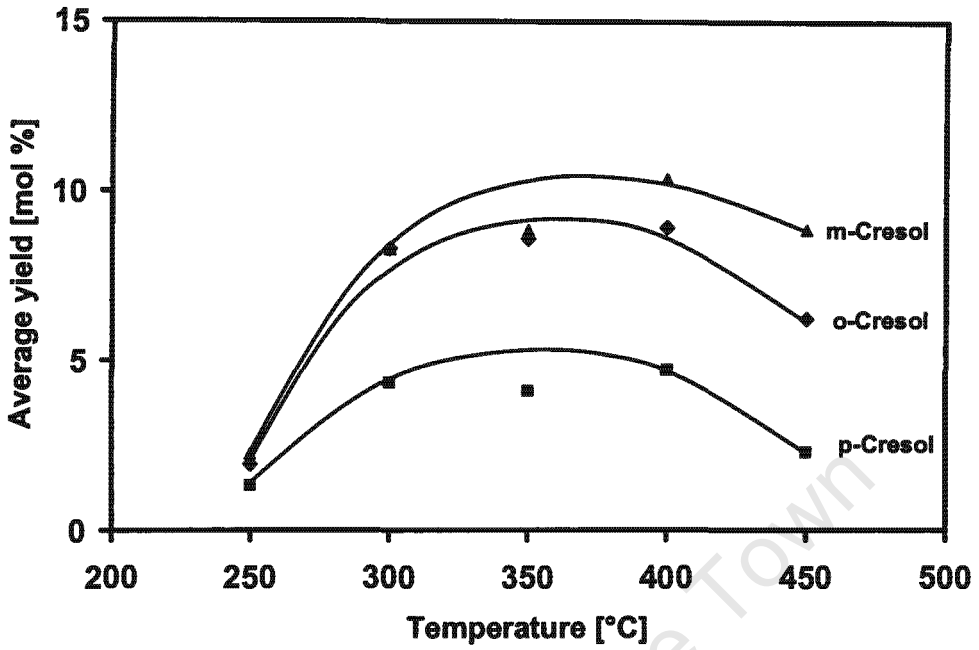


Figure 6-14 (Experiments 1 and 2): Average yield of cresol isomers versus temperature for a phenol : 2,5-xylenol feed mixture of molar ratio 1 : 1 over H-BEA-25 at a space velocity of 0.45 h^{-1}

Table 6-8 (Experiments 1 and 2): Distribution of the cresol isomers at different temperatures for a 1 : 1 molar phenol : 2,5-xylenol feed mixture over H-BEA-25 at a space velocity of 0.45 h^{-1}, and distribution in thermodynamic equilibrium

2,5-Xylenol Conversion (mol %)	*Temperature (°C)*					**Equilibrium Distribution at 380°C*
	250	300	350	400	450	
	40.7	71.3	78.0	74.7	55.9	
Compound	*Amount (mol %)*					
o-Cresol	35.3	39.7	39.9	37.2	35.8	36
p-Cresol	23.9	20.8	19.0	19.7	13.2	16
m-Cresol	40.8	39.6	41.1	43.2	51.0	48

* [Imbert et al., 1997, in gas phase and Fritsch et al., 2003, in liquid phase]

Figure 6-15 shows the yield of xylenol isomers with 2,4-xylenol being the most favoured product isomer throughout the range of temperature. A decreasing yield of 2,4- and a minimum of 2,5-xylenol yield with increasing temperature is seen. This was expected due to consumption of these isomers by increasing rate of transalkylation with increasing temperature (see figure 6-20) and the 2,5-xylenol yield reflects the maximum in conversion at about 350°C. A similar trend was expected with at least 2,6-xylenol and 3,5-xylenol since these are the other primary products from 2,5-xylenol isomerisation (figure 6-3). However, according to table 6-9 the yields of the other xylenol isomers (excluding 2,4- and 2,5-xylenol) seem to pass over maximums throughout the temperature range of the experiment mirroring the content of the feed isomer. Similar trends were observed with an experiment carried out with a different molar ratio of the feed components (figure 6-16). The reason for the yield of 2,4-xylenol not showing trends similar to the rest of the xylenol isomers yield with increasing temperature could possibly be explained by 2,4-xylenol being most easily formed at low temperatures and the approach to thermodynamic equilibrium (table 6-9). However, the latter cannot be checked and proofed due to the fact that varying equilibrium distributions are obtained from different sources as mentioned in section 6.7.1.1.

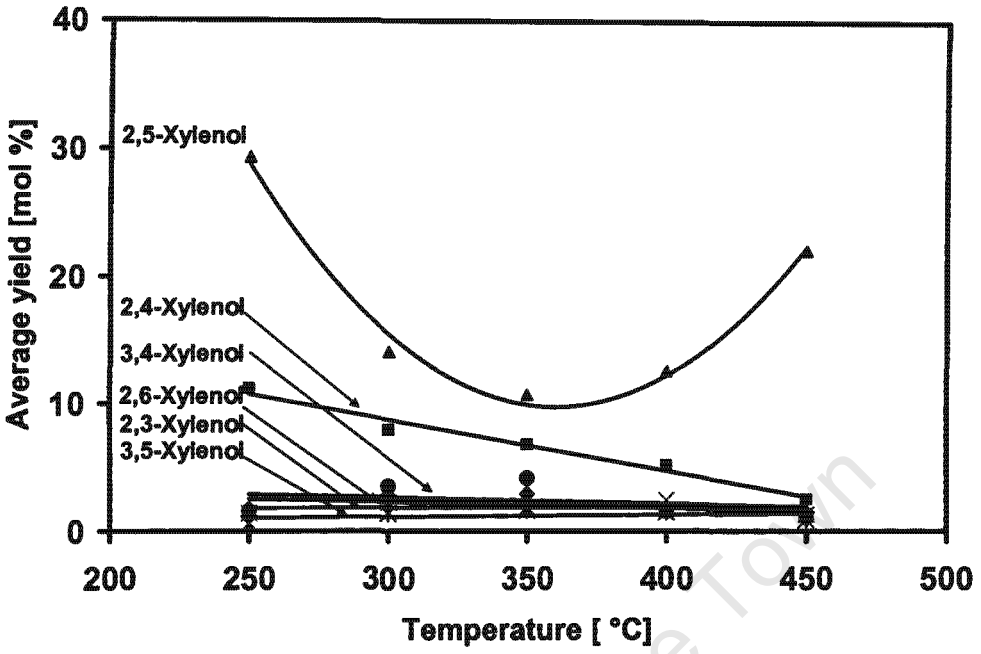


Figure 6-15 (Experiment 1 and 2): Average yields of xylenol isomers versus temperature for a phenol : 2,5-xylenol feed mixture of molar ratio 1 : 1 over H-BEA-25 at a space velocity of 0.45 h^{-1}

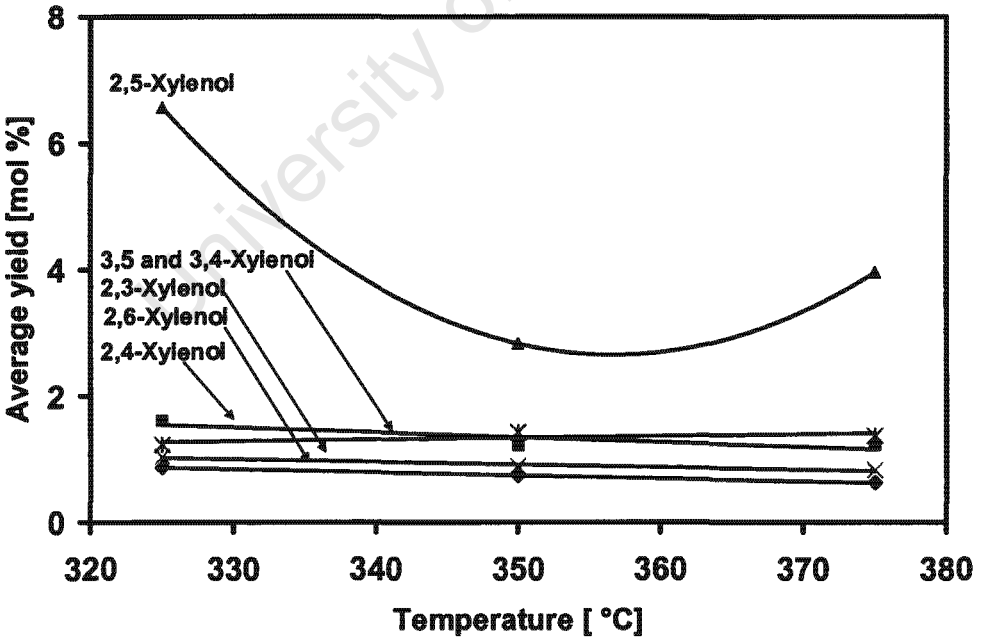


Figure 6-16 (Experiment 5): Average yields of xylenol isomers versus temperature for a phenol : 2,5-xylenol feed mixture of molar ratio 5 : 1 over H-BEA-25 at a space velocity of 0.113 h^{-1}

Table 6-9 (Experiments 1 and 2): Distribution of the xylenol isomers at different temperatures for a 1 : 1 molar ratio phenol : 2,5-xylenol feed mixture over H-BEA-25 at a space velocity of 0.45 h^{-1}, and distribution in thermodynamic equilibrium.

2,5-Xylenol Conversion (mol %)	*Temperature (°C)*					*Equilibrium Distribution at 350°C (mol %)*		
	250	300	350	400	450			
	40.7	71.3	78.0	74.7	55.9			
Compound	*Amount (mol %)*					*	**	***
2,6-Xylenol	3.8	8.7	10.4	7.1	3.4	12.9	11.1	10.9
2,4-Xylenol	24.5	24.9	24.4	20.7	8.6	43.5	29.6	21.1
2,5-Xylenol	64.1	44.1	38.2	50.3	75.9	17.7	23.7	29.4
2,3-Xylenol	3.0	7.0	6.5	9.7	4.5	3.6	8.9	10.2
3,5-Xylenol	1.3	4.3	5.8	5.9	3.1	16.3	14.1	15.0
3,4-Xylenol	3.4	11.0	14.8	6.2	4.5	6.1	12.6	13.4

*[Fernsby, 2006]

**[Pigman et al., 1954]

***[This work (figure 5-57)]

6.7.4 Ratio of isomerisation to transalkylation with changing conditions

The ratio of isomerisation to transalkylation increases with increasing space velocity as shown in figure 6-17. Increasing space velocity leads to decreasing residence time which in turn leads to decreasing conversion. This would affect transalkylation more than isomerisation since, as mentioned in section 6.7.2, isomerisation is a far more easy reaction than transalkylation in terms of activation energy and steric/geometrical requirements. This means that the thermodynamic equilibrium distribution of the xylenols is more closely approached, limiting 2,5-xylenol isomerisation conversion, while transalkylation, i.e. the carbon number distribution (see section 6.7.1.2) is further away from equilibrium, not yet limiting transalkylation conversion.

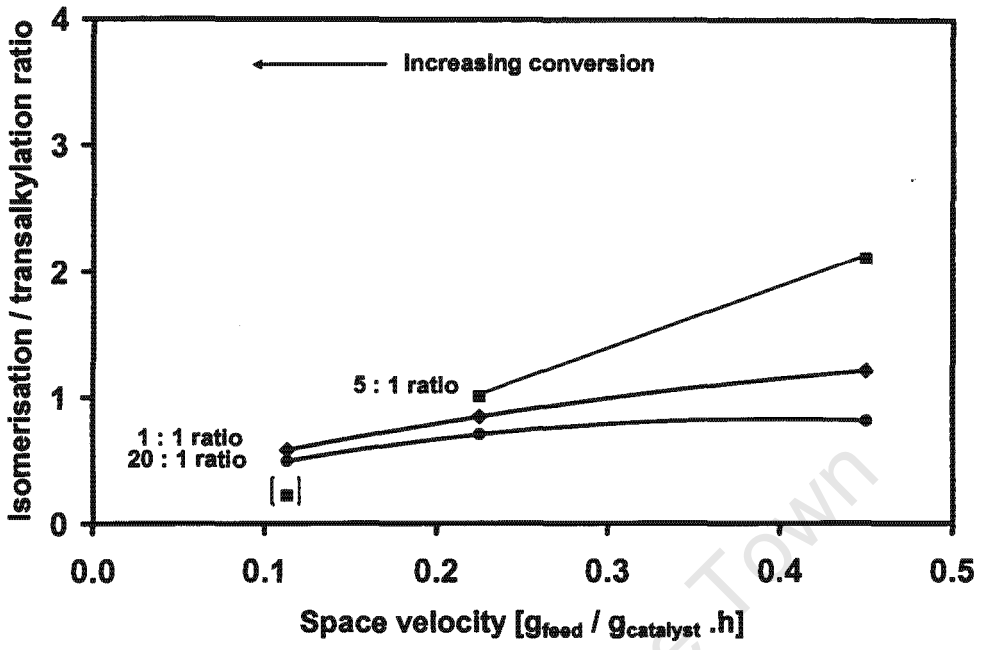


Figure 6-17 (Experiments 3, 7 and 8): Ratio of isomerisation to transalkylation of 2,5-xylenol versus space velocity for phenol : 2,5-xylenol feed mixtures of different molar ratios over H-BEA-25 at a temperature of 350°C

The ratio of isomerisation to transalkylation conversion decreases constantly with increasing temperature (figure 6-18). This indicates towards higher activation energy of the transalkylation reaction and hence makes it comparably easier for this reaction to take place at elevated temperatures. This trend seems to hold, regardless of the significant data scatter, over the entire temperature range studied (250°C – 450°C), as expected, regardless that conversion is passing over a maximum at 350°C and declining above of this temperature (see figures 5-3 and 5-44).

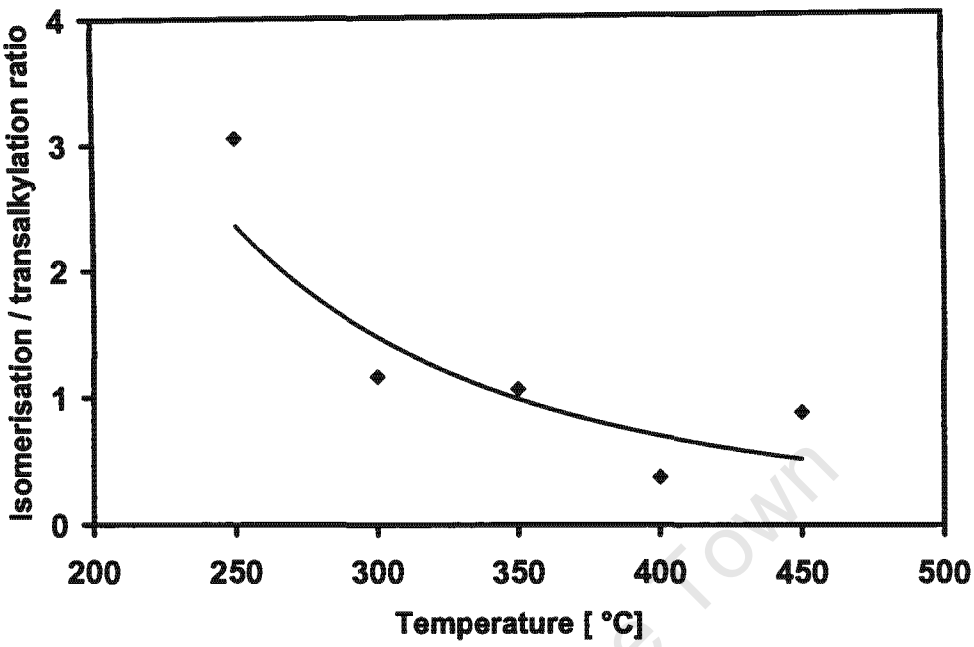


Figure 6-18 (Experiments 1 and 2): Ratio of isomerisation to transalkylation of 2,5-xylenol versus temperature for a phenol : 2,5-xylenol feed mixture of molar ratio 1 : 1 over H-BEA-25 at a space velocity of 0.45 h^{-1}

A slight trend is seen from the plot of ratio of isomerisation to transalkylation versus changing the phenol : 2,5-xylenol molar ratio (figure 6-19). It would have been expected that the ratio of isomerisation to transalkylation would decrease with increasing phenol : 2,5-xylenol ratio for reasons discussed in section 6.7.1. However, figure 6-6 shows that the yields of isomerisation and transalkylation products are each almost unaffected by the feed ratio and thus their ratios (figure 6-19) supporting the conclusion drawn in section 6.7.1 that transalkylation in liquid phase is closer to first than second.

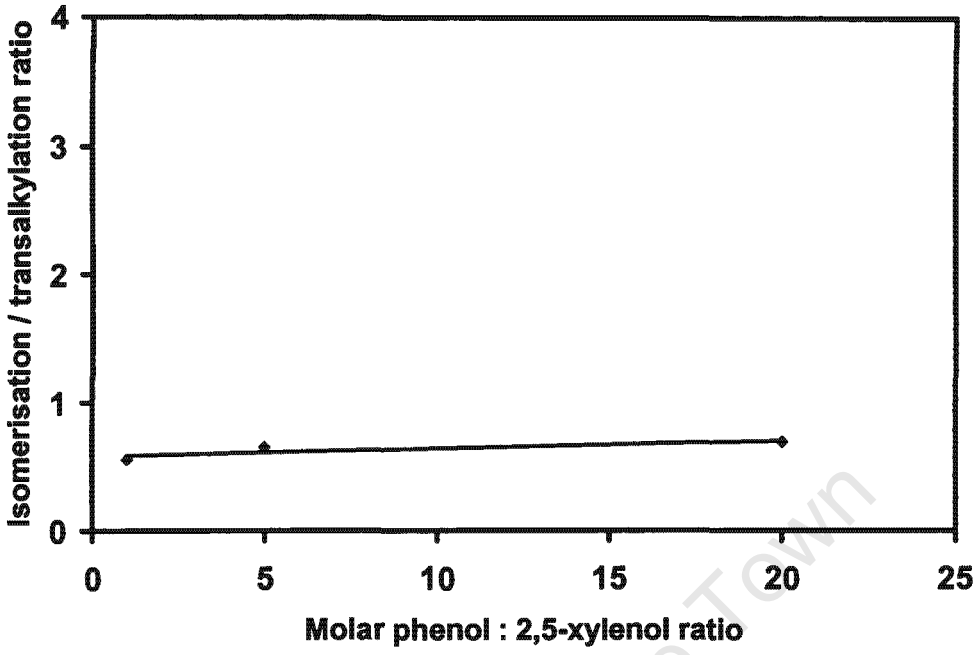


Figure 6-19 (Experiments 3, 7 and 8): Ratio of isomerisation to transalkylation versus molar phenol : 2,5-xylenol feed ratio over H-BEA-25 at a temperature of 350°C and a space velocity of 0.113 h^{-1}

6.8 Reactions of higher methylphenols with phenol

6.8.1 Reaction of phenol with 2,3,6-trimethylphenol

2,3,6-trimethylphenol was found to undergo a transalkylation reaction with phenol. This was shown by the presence of xylenols and cresols in the product spectrum (see figure E1 in appendix E, and figures 5-52 and 5-53). Yields and selectivities of cresols and xylenols are more or less parallel in their variation with changing 2,3,6-trimethylphenol conversion and, on a molar basis, differ only slightly (figure 5-52 and 5-53). This was expected because each trimethylphenol molecule reacting with a phenol molecule would yield exactly one molecule of cresol and another molecule of xylenol as shown in figure 3-1. However, molar xylenol selectivity, always being somewhat higher than molar cresol selectivity, indicates towards disproportionation reactions in the trimethylphenol fraction (with co-product tetramethylphenols as part of the 'heavies').

The conversion of 2,3,6-trimethylphenol was found to be much higher than that of phenol at all space velocities applied (figure 5-50). This is simply because, as in the case of phenol and 2,5-xylenol (see section 6.4), 2,3,6-trimethylphenol can be converted in more ways than phenol. Phenol can essentially only undergo transalkylation with 2,3,6-trimethylphenol but 2,3,6-trimethylphenol can also undergo isomerisation, which is even the much easier reaction. As a result, a much higher conversion is obtained with 2,3,6-trimethylphenol than with phenol.

Selectivities for all product fractions apart from other trimethylphenol isomers were found to increase with increasing 2,3,6-trimethylphenol conversion (see figure 5-52). The reason for the decrease in 'other 2,3,6-trimethylphenol isomers' selectivity is the same as discussed in section 6.4.2 for decreasing selectivities of 'other 2,5-xylenol isomers' with increasing conversion, namely consumption of all of the individual isomers in transalkylation reactions.

6.8.1.1 Distribution of cresol and xylenol isomers obtained from reacting phenol with 2,3,6-trimethylphenol

Reacting phenol and 2,3,6-trimethylphenol at different space velocities over H-BEA-25 at 350°C resulted in o-cresol being the isomer with the highest yield at all space velocities applied as shown in figure 6-20, while p-cresol and m-cresol show rather equal but lower yields. Figure 6-17 and table 6-10 show that the m-cresol content in the cresol fraction from transalkylating trimethylphenol with phenol is indeed significantly lower, less than half that obtained from transalkylating xylenol. This has mechanistic reasons that will be discussed in detail in section 6.9. The individual yields obtained show clearly that the cresol distribution is far from thermodynamic equilibrium (see table 6-10) but the yield of m-cresol increases steepest when space velocity is reduced, indicating secondary isomerisation.

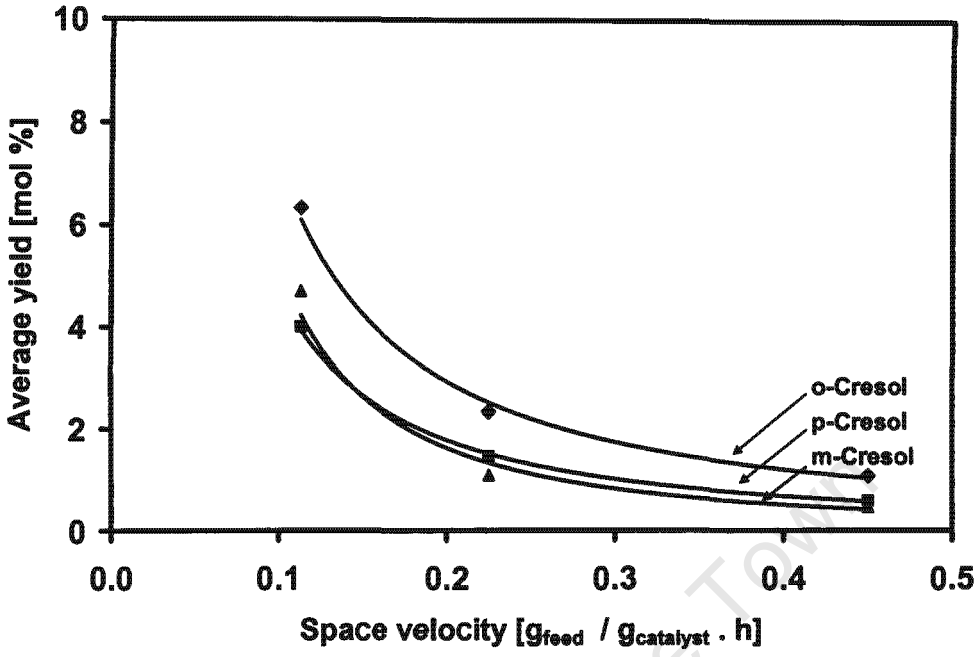


Figure 6-20 (Experiment 6): Average yields of cresol isomers versus space velocity for a phenol : 2,3,6-trimethylphenol feed mixture of molar ratio of 1 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-10 (Experiment 6): Distribution of the cresol isomers at different space velocities for a 1 : 1 molar ratio phenol : 2,3,6-trimethylphenol feed mixture over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium.

2,3,6-Trimethylphenol Conversion (mol %)	*Space velocity (WHSV) h^{-1}*			**Equilibrium Distribution at 380°C*
	0.113	**0.225**	**0.45**	
	74.6	55.5	69.5	
Compound	***Amount (mol %)***			
o-Cresol	42.1	47.9	50.6	36
p-Cresol	26.6	29.9	27.6	16
m-Cresol	31.2	22.2	21.5	48

* [Imbert et al., 1997, in gas phase and Fritsch et al., 2003, in liquid phase]

Reacting phenol with 2,3,6-trimethylphenol results in 2,5-xylenol becoming the xylenol isomer formed with the highest yield at low space velocity as shown in figure 6-21, for which the trend reflects probably an approach towards thermodynamic equilibrium distribution. The xylenol isomer distribution is shown in table 6-11. As In the case of the xylenol distribution obtained from 2,5-xylenol conversion (section 6.7.1.1) nothing else can be deduced from this distribution with regard to approach to equilibrium with changing space velocity.

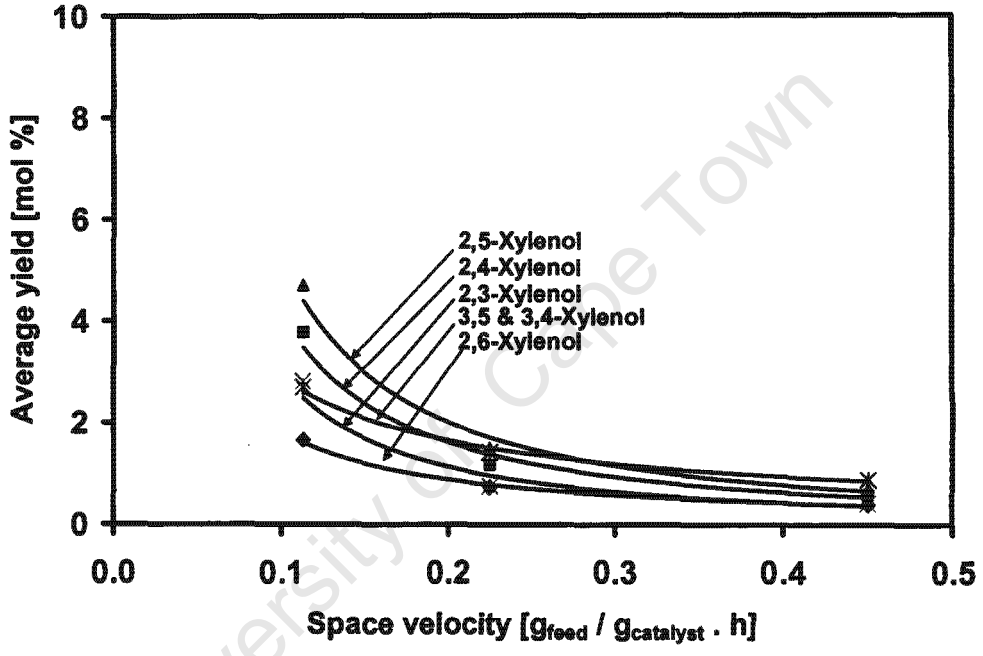


Figure 6-21 (Experiment 6): Average yields of xylenol isomers versus space velocity for a phenol : 2,3,6-trimethylphenol feed mixture of molar ratio of 1 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-11 (Experiment 6): Distribution of the xylenol isomers at different space velocities for a 1 : 1 molar ratio phenol : 2,3,6-trimethylphenol feed mixture over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium.

2,5-Xylenol Conversion (mol %)	*Space velocity (WHSV) h^{-1}*			*Equilibrium Distribution at 350°C (mol %)*		
	0.113	**0.225**	**0.45**			
	74.6	55.5	69.5			
Compound	*Amount (mol %)*			*	**	***
2,6-Xylenol	10.6	13.2	13.1	12.9	11.1	10.9
2,4-Xylenol	24.1	21.0	19.7	43.5	29.6	21.1
2,5-Xylenol	30.1	26.9	23.7	17.7	23.7	29.4
2,3-Xylenol	18.0	13.5	14.0	3.6	8.9	10.2
3,5-Xylenol	17.2****	25.4****	29.6****	16.3	14.1	15.0
3,4-Xylenol				6.1	12.6	13.4

*[Fernsby, 2006]

**[Pigman et al., 1954]

***[This work (figure 5-57)]

****Peaks not separated in GC trace

6.8.2 Reaction of phenol with the simulated technical mixture

The ultimate object of this study was to reduce the average carbon number of a simulated technical mixture of higher methylated phenols by transalkylation with phenol. The target compounds were essentially tetramethylphenols and trimethylphenols. The objective would have been achieved if a large amount of these target compounds could be converted to cresols and xylenols.

Part of the objective was achieved in that most of the tri- and tetramethylphenols were consumed during reaction (compare tables 5-2 – 5-4). About 60% of the trimethylphenols and around 80% of the tetramethylphenols were converted under the conditions applied with conversion still moderately increasing towards

lower space velocities (figure 5-54). The other part of the objective was achieved in that significant amounts of cresols and also xylenols were formed (table 5-4 and figures 5-55 and 5-56). Note the high excess of phenol in the reaction and product mixtures when judging the yields.

Selectivity and yield towards cresols were found to increase significantly with decreasing space velocity. Given the 20 : 1 molar surplus of phenol over the simulated technical mixture, cresols represent the major and final product of the transalkylation reaction sequence, starting from phenol.

The selectivity and yield of xylenols (see figures 5-55 and 5-56) seem to be unaffected by changing space velocity. This reflects the role of the xylenols as intermediates in the reaction sequence from tetramethylphenols to cresols. The same appears to hold for the trimethylphenols, according to data given in tables 5-2 to 5-4.

An OH-group balance over the reaction mixture of phenol and the simulated technical mixture and the product mixture (reactor effluent) is given in table 6-12. The result, with a deviation of -2.7% of the OH-group content in the product compared to the OH-groups that were fed, confirms the product analysis and also that the assumption is quite right to assign a single OH-group to the unidentified molecules of 'others'.

It should be noted that between half and two thirds of the consumed OH-groups from phenol goes into diphenylethers, mostly from the parent compound itself.

Table 6-12 (Experiment 9): OH-group balance for the conversion of the phenol : simulated technical mixture feed of ca. 20 : 1 molar ratio over H-BEA-25 at 350°C and a space velocity of 0.11 h^{-1}

Compound	*OH (in) mol %*	*OH (out) mol%*	*Difference*
Phenol	94.17	54.41	-39.76
Cresols	0.47	10.13	+9.66
Xylenols	0.85	2.74	+1.89
Trimethylphenols	2.51	1.30	-1.21
Tetramethylphenols	0.94	0.08	-0.86
Ethers*	-	19.99	+19.99
Others**	0.93	11.47	+7.59
TOTAL	**99.87**	**100.12**	**-2.7**

* Considered as representing two moles of phenol or alkyl phenol, i.e., the bridging O in the ether and an OH in water

$$2\ phenol \rightarrow 1\ diphenylether + water$$

** Assumed to carry a single OH-group per molecule on average.

6.8.2.1 Distribution of cresol and xylenol isomers obtained from reacting the simulated technical mixture with phenol

Figure 6-22 and table 6-13 show that a similar trend is obtained as in the case of 2,3,6-trimethylphenol with regard to cresol isomer yields (section 6.6.1.1). Isomer distribution at high space velocity is dominated by o-cresol, with about half as much m-cresol and p-cresol forming, and a trend towards higher m-cresol content, i.e. towards thermodynamic equilibrium, as space velocity decreases.

It should be noted that in this case the conversion was based on tetramethylphenols. This is because tetramethylphenols are being consumed and not formed unlike the lower methylphenols which are being consumed and formed at the same time and hence cannot be used as a measure of conversion.

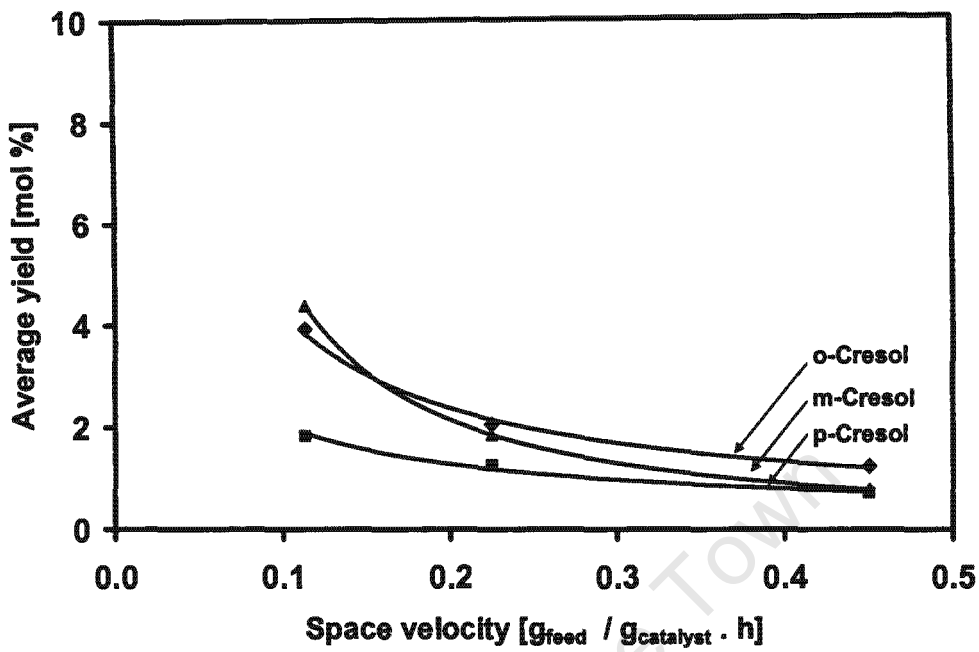


Figure 6-22 (Experiment 9): Average yields of cresol isomers versus space velocity for a phenol : simulated technical mixture feed of molar ratio of ca. 20 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-13 (Experiment 9): Distribution of the cresol isomers at different space velocities for a phenol : simulated technical mixture feed of ca. 20 : 1 molar ratio over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium.

Tetramethylphenols Conversion (mol %)	*Space velocity*			**Equilibrium Distribution at 380°C*
	0.113	**0.225**	**0.45**	
	91.3	85.4	67.6	
Compound	***Amount (mol %)***			
o-Cresol	38.7	39.8	45.2	36
p-Cresol	18.1	24.3	26.1	16
m-Cresol	43.2	35.8	28.7	48

* [Imbert et al., 1997, in gas phase and Fritsch et al., 2003, in liquid phase]

From the simulated technical mixture's reaction with phenol, 2,4-xylenol and 3,4-xylenol are formed with highest yields at high space velocity (figure 6-23). Towards lower space velocity the xylenol isomer distribution would be expected to tend towards thermodynamic equilibrium. However, as in the case of the other co-feeds, no conclusion can be made about the xylenol isomer distribution shown in the figure and table 6-14 and with regard to approach to equilibrium (as discussed in section 6.7.1.1).

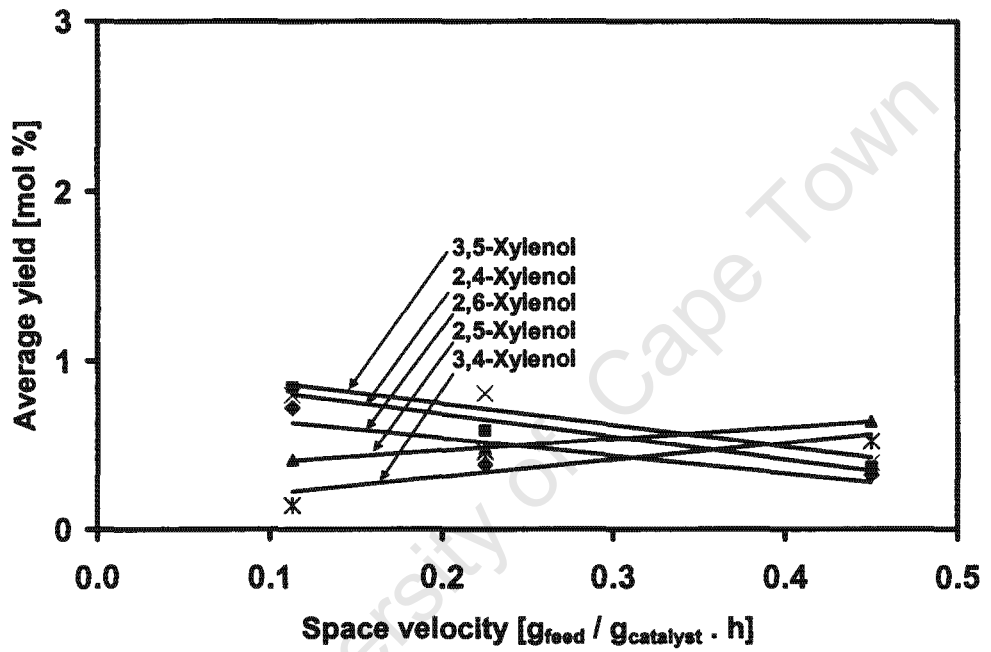


Figure 6-23 (Experiment 9): Average yield of xylenol isomers versus space velocity for a phenol : simulated technical mixture feed of molar ratio of ca. 20 : 1 over H-BEA-25 at a temperature of 350°C

Table 6-14 (Experiment 9): Distribution of the xylenol isomers at different space velocities for a phenol : simulated technical mixture feed of molar ratio of ca. 20 : 1 over H-BEA-25 at a temperature of 350°C, and distribution in thermodynamic equilibrium

Tetramethylphenols Conversion (mol %)	*Space velocity (WHSV) h^{-1}*			*Equilibrium Distribution at 350°C (mol %)*		
	0.113	0.225	0.45			
	91.3	85.4	67.6			
Compound	*Amount (mol %)*			*	**	***
2,6-Xylenol	23.7	13.6	13.6	12.9	11.1	10.9
2,4-Xylenol	27.7	20.9	15.7	43.5	29.6	21.1
2,5-Xylenol	13.4	17.0	27.3	17.7	23.7	29.4
2,3-Xylenol	26.1	28.7	16.8	3.6	8.9	10.2
3,5-Xylenol	4.6	16.3	22.3	6.1	14.1	15.0
3,4-Xylenol	4.6	3.4	4.3	16.3	12.6	13.4

*[Fernsby, 2006]

**[Pigman et al., 1954]

***[This work (figure 5-57)]

6.9 Reaction pathways of transalkylation and isomerisation / transalkylation

The overall reaction network of conversion of the phenol / 2,5-xylenol feed has been briefly discussed in section 6.4 and is shown in figure 6-1. It was shown in section 6.4.7 that 2,5-xylenol isomerises rather readily, while the transalkylation reaction with phenol is slower (figures 6-17 and 6-18). Even more so is the disproportionation reaction of two xylenol molecules, indicated by the very low selectivity to trimethylphenols (see for instance figure 5-4).

It was also shown in section 6.4 that not only 2,5-xylenol itself but also the other xylenol isomers that form undergo transalkylation with phenol (and presumably also amongst each other) and that way contribute to cresol formation. It can be

assumed that this holds throughout, i.e., also for the isomers forming from 2,3,6-trimethylphenol during the conversion of the phenol / 2,3,6-trimethylphenol feed mixture and the polymethylphenols in the feed made up from phenol and the simulated technical mixture.

With phenol / 2,5-xylenol feeds, cresols are both primary methylation and demethylation products, i.e. it cannot be distinguished whether an individual isomer origins from the phenol or a xylenol. However, this is distinguishable in case of the phenol / 2,3,6-trimethylphenol feed where, at low conversion, the cresols are the primary methylation products of phenol and the xylenols are the primary demethylation products of trimethylphenols.

6.9.1 Orientation of transalkylation with 2,3,6-trimethylphenol

At low conversion demethylation products would mostly originate from the feed isomer itself, 2,3,6-trimethylphenol, while other trimethylphenol isomers would considerably contribute at high conversion. Therefore the transalkylation product distribution obtained at low conversion should allow of a conclusion on the preferred positions on the rings for both the methylation and the demethylation step in the transalkylation mechanism to occur.

Figure 6-24 shows that – in ideal case, that is with kinetic preference for the o- and p-positions, following basic (chemical) selectivity rules – o- and p-cresol would be the products expected in 2 : 1 molar ratio from transferring a methyl group onto the phenol co-feed molecule (the methyl acceptor), regardless of the nature of the methyl donor, i.e. the polymethylphenol feed constituent, as long as the latter was a C_{9+}-phenol, meaning that it does not itself produce cresols by the first step of demethylation. It is obvious from figure 6-24 that m-cresol is not a primary product of transalkylation reactions of C_{9+}-polymethylphenols with phenol but would only form secondarily via 1,2-methyl shift isomerisation of the o- and p-

isomers or in secondary transalkylation steps between phenol and product xylenols.

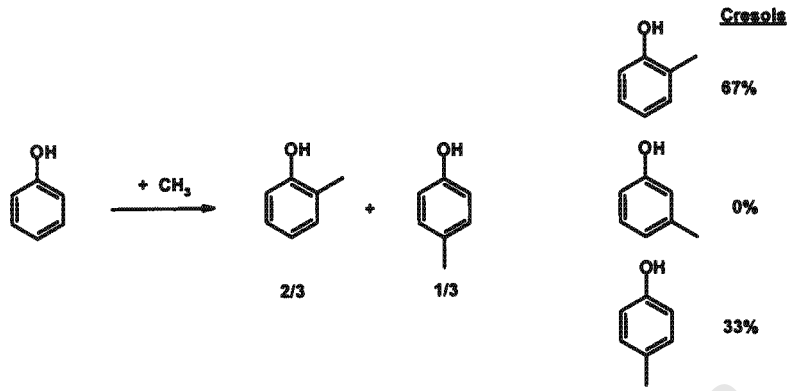


Figure 6-24: Products from phenol methylation via transalkylation with higher methylated phenols C_{9+}. Product distribution reflects basic (chemical) selectivity rules. 'CH_3' stands for the transferred methyl group

Table 6-10 shows indeed that at the highest space velocity applied the percentage of m-cresol in the cresols fraction is low, only 21.5 mol %, which is less than half of the percentage of o-cresol and its percentage in thermodynamic equilibrium. The o- / p-cresol ratio is 1.83, indeed close to the expected value of 2 (see figure 6-24).

With decreasing space velocity, i.e. increasing conversion and contribution of secondary (isomerisation and transalkylation) reactions, the distribution of the cresols tends towards thermodynamic equilibrium distribution, which results in increasing m-cresol content in particular (table 6-10). Isomerisation of the 2,3,6-trimethylphenol feed molecule prior to transalkylation should only influence the xylenol isomers distribution, not that of the cresols (under 'basic' selectivity rules).

Figure 6-25 shows the reaction pathways and the primary products from transalkylating 2,3,6-trimethylphenol with phenol. Anticipating 'ideal' selectivity following basic (chemical) rules, namely the groups in o-positions being reactive but not the group in the m-position, the resulting xylenols should only be the

2,3- and the 2,5-isomer, forming with equal selectivity (see middle column in table 6-15).

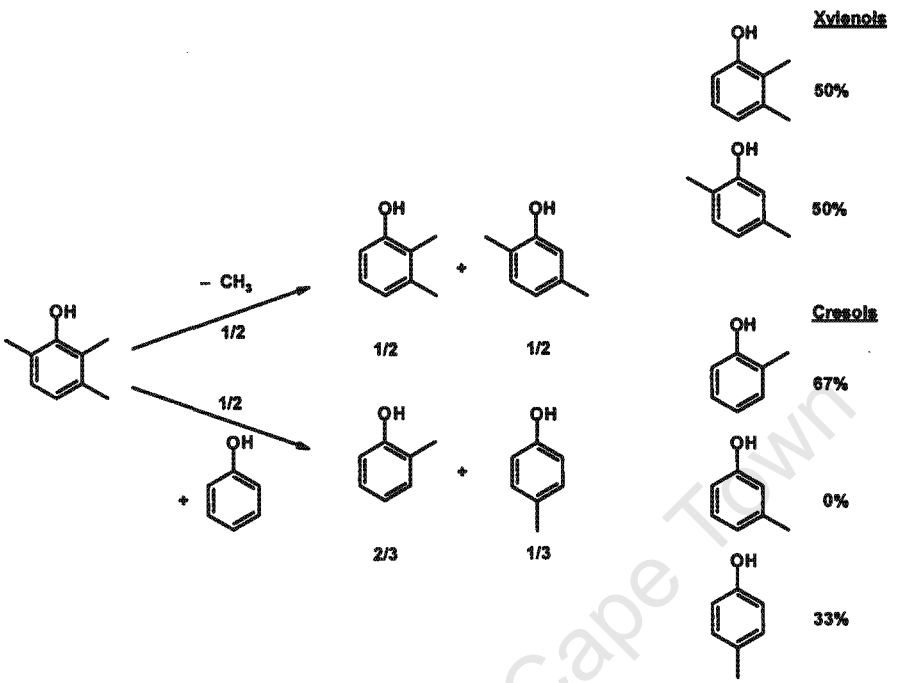


Figure 6-25: Reaction pathways and expected product distribution from transalkylating 2,3,6-trimethylphenol with phenol, applying basic (chemical) selectivity rules. 'CH_3' stands for the transferred methyl group

Table 6-15: Expected isomer distribution in the xylenol product fraction from trimethylphenol (TMP) transalkylation with phenol depending on the degree of primary isomerisation of the fed 2,3,6-trimethylphenol isomer when applying basic (chemical) selectivity rules for the demethylation step

	Trimethylphenols distribution in reaction mixture (mol %)	
	Pure 2,3,6-TMP	2,3,6- : 2,3,5- : 2,4,6-TMP = 2 : 1 : 1
Compound	***Ideal distribution in product mixture (mol %)***	
2,6-Xylenol		8
2,4-Xylenol		16
2,5-Xylenol	50	25
2,3-Xylenol	50	25
3,4-Xylenol		0
3,5-Xylenol		25

In figure 6-26 the transalkylation pathways are illustrated of the primary 1,2-methyl shift isomerisation products of 2,3,6-trimethylphenol, namely 2,3,5- and 2,4,6-trimethylphenol. This would result in three of the other xylenol isomers forming additionally, namely 2,4-, 2,6- and 3,5-xylenol but not the 3,4-isomer. Assuming, for instance, a 2 : 1 : 1 contribution of the original and each of the primarily forming trimethylphenol isomers to the final transalkylation product would result in a xylenol isomer distribution as given in table 6-15, last column.

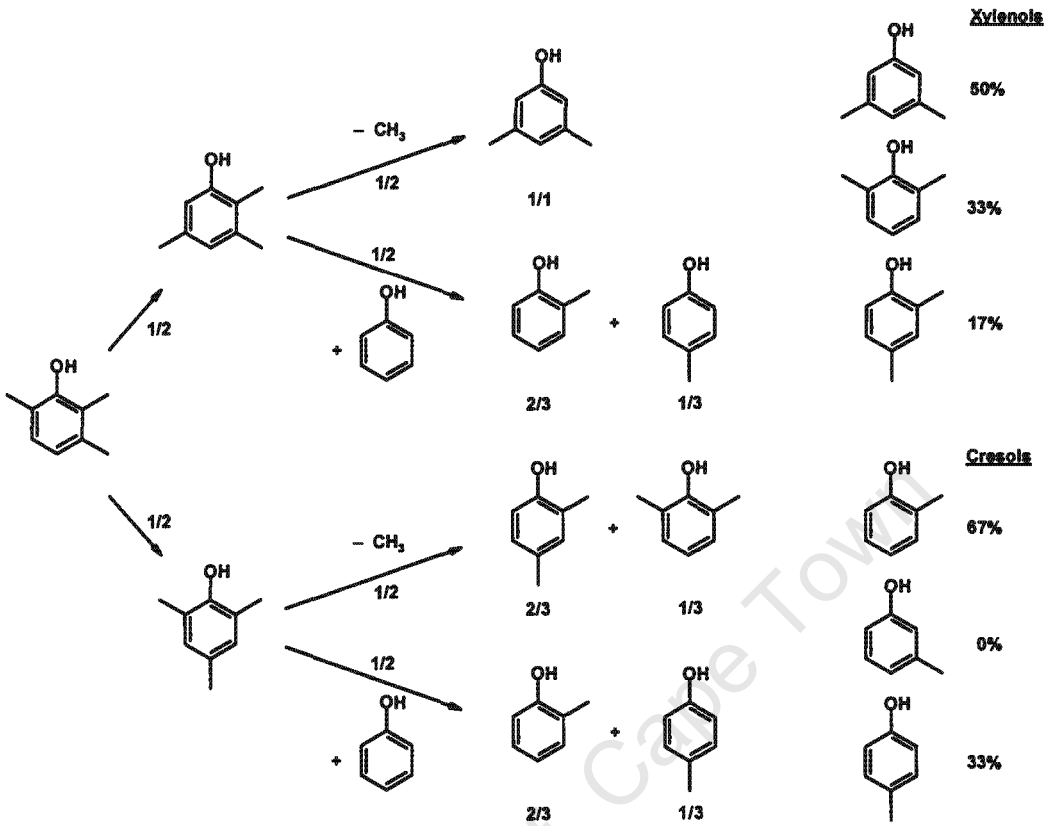


Figure 6-26: Reaction pathways and expected product distribution from transalkylating the primarily forming isomers of 2,3,6-trimethylphenol with phenol, applying basic (chemical) selectivity rules. 'CH_3' stands for the transferred methyl group

Indeed, the theoretical xylenol distributions, such as given in table 6-15, are to some extend reflected in the experimentally obtained xylenol distributions, particularly at the highest space velocity applied, table 6-11, however, the observed trends make any sense yet with respect to kinetic control of the isomers distribution or approach to thermodynamic equilibrium at low space velocities.

6.9.2 Orientation of transalkylation with 2,5-xylenol

The transalkylation reaction between 2,5-xylenol and phenol produces only cresols, be it by methyl addition to phenol, be it by methyl abstraction from the 2,5-xylenol, see figure 6-27. Following 'basic' (chemical) selectivity rules, the cresol distribution should be as indicated in the figure, namely 33 % o-, 50 %

m- and 17 % p-cresol. This distribution would be expected at very low conversion, however, this range was beyond the scope of the experiments. However, note that this very primary distribution of the cresols, as given in figure 6-27 and table 6-16, is very similar to the distribution in thermodynamic equilibrium (see for instance table 6-1), though kinetically controlled.

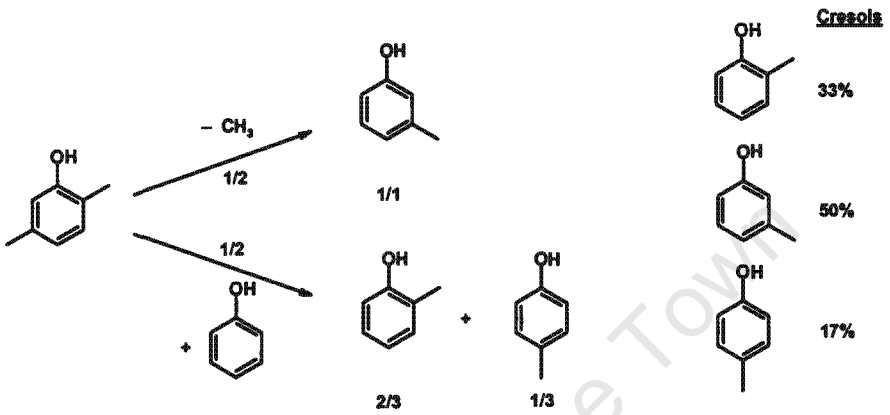


Figure 6-27: Reaction pathways, products and expected product distribution from transalkylating 2,5-xylenol with phenol, applying basic (chemical) selectivity rules. 'CH_3' stands for the transferred methyl group

Including the isomers that origin from initially formed 1,2-shift isomerisation products of 2,5-xylenol, see figures 6-28 a – c, makes the distribution of the cresols dominated by o-cresol, see table 6-16. Eventually, under severe conditions, the cresol distribution should approach thermodynamic equilibrium (table 6-1) with values that are close again to those expected under kinetic control at very low conversion.

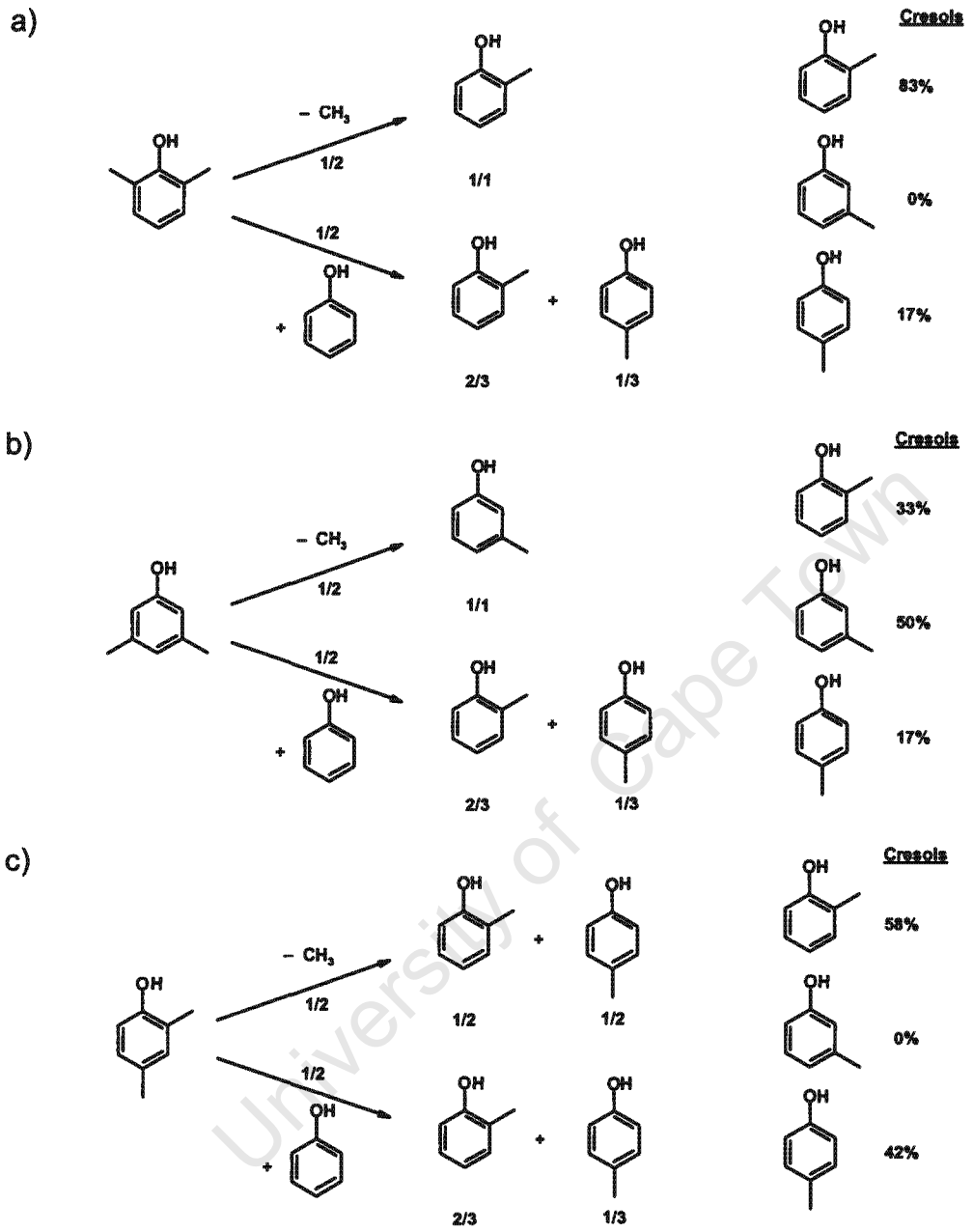


Figure 6-28: Reaction pathways, products and expected product distribution from transalkylating the primary 1,2-methyl shift isomers from 2,5-xylenol (a – c) with phenol, applying basic (chemical) selectivity rules. 'CH_3' stands for the transferred methyl group

Table 6-16: Expected isomer distribution in the cresol product fraction from xylenol transalkylation with phenol depending on the degree of isomerisation of the fed 2,5-xylenol isomer when applying basic (chemical) selectivity rules for the demethylation and methylation steps

	Xylenol distribution in reaction mixture (mol %)	
	Pure 2,5-Xylenol	2,5- : 2,6- : 2,4- : 3,5-Xylenol = 3 : 1 : 1 : 1
Compound	***Ideal distribution in product mixture (mol %)***	
o-Cresol	33	46
p-Cresol	17	21
m-Cresol	50	33

Indeed, though not very pronounced and clear, it appears from tables 6-1, 6-3 and 6-5 that the percentages of o-cresol and m-cresol pass through maxima and minima, respectively, as a function of reaction severity.

As in the case of 2,3,6-trimethylphenol transalkylation, the xylenol product distribution obtained from 2,5-xylenol isomerisation during transalkylation at high severity appears to not reflect equilibrium distributions or exhibit any consistent trend in this direction, see tables 6-2, 6-4 and 6-6.

At the moment selectivities and trends within the xylenol fractions from transalkylation of phenol with higher methylated phenols are not understood and can not be explained, with the possible exception of the high space velocity, medium conversion product from 2,3,6-trimethylphenol transalkylation with phenol, see section 6.9.1 and table 6-9.

6.9.3 Orientation of transalkylation with the simulated technical mixture

The cresols obtained from transalkylating the simulated technical mixture with phenol (see table 6-13) are essentially phenol methylation products, given the

huge increase in cresol content in the product compared to the feed (see tables 5-2 – 5-4).

High o-cresol and low m-cresol contents are found, which, indeed, correspond to the theoretically derived, kinetically controlled distributions (figure 6-24) and to the cresol fraction obtained from transalkylation of phenol with trimethylphenol (table 6-10).

Again, no conclusive interpretation is possible of the obtained xylenol distributions (table 6-14).

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

The objective of this research was to demonstrate that the transformation is possible of low value mixed polymethylphenols (C_{9+}), which will be produced in the near future in increasing amounts from extracting the naphtha by-product stream from Sasol's South African coal gasification operations, into high value cresols and xylenols via transalkylation with phenol over acid zeolite catalysts, and with commercially attractive selectivity, conversion, rate and catalyst lifetime.

The results of this study, though just marking a first step towards developing such a process, are very promising, in so far as:

- The transformation works.
- The valuable aromatic (phenolic) OH-groups present in the constituents of a C_{9+}-phenols fraction can be recovered.
- The C_{9+}-phenols, due to the activation of their aromatic rings by the OH-group, provide a cheap and active reagent for the methylation of phenol.
- A commercially available acid zeolite catalyst was found, of the wide pore H-BEA type, which shows a reasonable activity, selectivity and life time.
- Apparently high excess of phenol is not required nor recommended to achieve a satisfactory product carbon number distribution.

Less favourable aspects of the process that surfaced are the following:

- The isomers distribution in the cresol fraction is kinetically controlled with a higher percentage of low market value o-cresol and a lower percentage of high market value m-cresol than in thermodynamic equilibrium.
- The once through yield of cresol (relative to the C_{9+} feed component) is thermodynamically limited by carbon number equilibrium distribution corresponding to the given excess of phenol.

- Between half and two third of the converted phenol reacts to diphenylether which would be a significant loss of OH-groups and aromatic rings.
- Recycling of unconverted feed and certain product compounds is required.
- Significant percentages of heavies build-up when operating at too high a reaction temperature (above about 375°C).

The aforementioned less favourable aspects should be addressed in a subsequent study as follows:

- Increasing the once through yield of cresols from the C_{9+} fraction is an issue of the phenol content in the feed (paying the price in form of larger volumes to handle, increased ether formation and increased recycle ratios).
- Maximising the cresol yield or the percentage of m-cresol in the cresol fraction, respectively. This is an issue of reaction severity (paying the price in form of shorter catalyst lifetime and making more heavies).
- Limiting the high selectivity towards diphenylether through recycling, that way avoiding net production of diphenylether (paying the price in form of increased recycle ratios).
- Limiting the high selectivity towards diphenylethers by applying a lower excess of phenol in order to slow down ether formation (paying the price in form of lower cresol and xylenol selectivities).
- Limiting the high selectivity towards diphenylethers by addition of water in order to push back thermodynamic equilibrium ether concentration (paying the price in form of e.g. lower catalyst activity and larger quantities to handle).
- Keeping the build-up of heavies at bay through operating at not to high reaction temperatures, below about 375°C (paying the price in form of low reaction rates).

With respect to a final judgement of the suggested process it should be noted that the alternative 'direct' routes to cresols, namely, the alkylation of phenol with

methanol, are not 'clean' at all, requiring rather severe conditions, in particular when high selectivity towards m-cresol is aimed at.

Chapter 8

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Appendices

Appendix A: Physical properties of the compounds used in the study

Table A1: Physical properties of phenol [Fiege, 2003]

Molecular weight	94.11 g/mol
Boiling point (101.3 kPa)	181.75 °C
Melting point (101.3kPa)	40.9 °C

Table A2: Physical properties of cresols [Fiege, 2003]

Molecular weight	108.14 g/mol
Boiling point (101.3 kPa)	
o-cresol	191 °C
m-cresol	202.23 °C
p-cresol	201.94 °C
Melting point (101.3 kPa)	
o-cresol	30.99 °C
m-cresol	12.22 °C
p-cresol	34.69 °C

Table A3: Physical properties of xylenols [Fiege, 2003]

Molecular weight	122.16 g/mol
Boiling point (101.3 kPa)	
2,3-xylenol	216.87 °C
2,4-xylenol	210.93 °C
2,5-xylenol	211.13 °C
2,6-xylenol	201.03 °C
3,4-xylenol	266.95 °C
3,5-xylenol	221.69 °C
Melting point (101.3 kPa)	
2,3-xylenol	75.57 °C
2,4-xylenol	25.54 °C
2,5-xylenol	74.85 °C
2,6-xylenol	45.62 °C
3,4-xylenol	65.11 °C
3,5-xylenol	63.27 °C

Table A4: Physical properties of trimethylphenols [Fiege, 2003]

Molecular weight	136.19 g/mol
Boiling point (101.3 kPa)	
3,4,5-trimethylphenol	248 °C
2,3,4-trimethylphenol	235-237 °C
2,4,5-trimethylphenol	232 °C
2,4,6-trimethylphenol	220 °C
2,3,5-trimethylphenol	230-231 °C
2,3,6-trimethylphenol	236 °C
Melting point (101.3 kPa)	
3,4,5-trimethylphenol	109 °C
2,3,4-trimethylphenol	81 °C
2,4,5-trimethylphenol	72 °C
2,4,6-trimethylphenol	71-74 °C
2,3,5-trimethylphenol	92-95 °C
2,3,6-trimethylphenol	62-64 °C

Appendix B: Calibration of mass flow controller

The Brooks thermal mass flow controller that was used (FIC-122 in figure 4-1) needed to be calibrated so as to be able to accurately determine the amount of nitrogen flowing through it at any time. The flow through the mass flow controller is measured on a percentage basis, with 100% representing maximum flow. The calibration is hence needed to be able to set the percentage flow for any flow in cm^3/s that is required. The calibration was done by choosing a number of set points and measuring the corresponding volumetric flow for each set point, using a bubble flow meter. From these pairs of values, a graph of volumetric flow (cm^3/s at 20°C) versus percentage flow (%) was plotted.

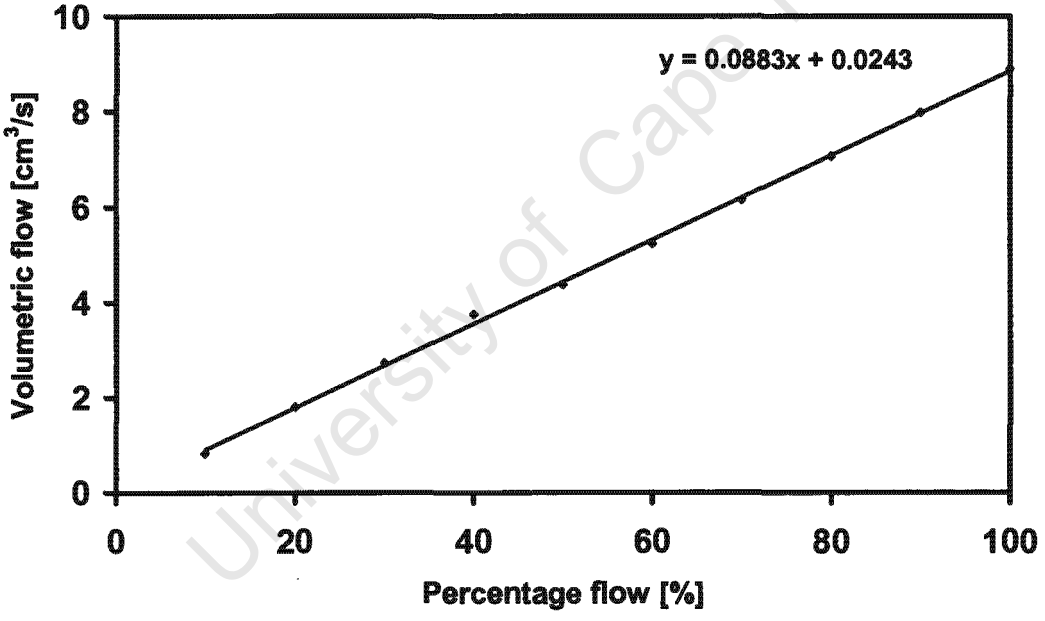

Figure B1: Volumetric flow (cm^3/ s, NPT) versus percentage flow (%) for mass flow controller calibration

From this plot, the following relationship was obtained.

Set point (%) = (Volumetric flow (cm^3/s) – 0.024)/0.088

Appendix C: Calculation of relative rates and mol fraction for comparison

The relative changes that would be expected from elemental second order rate laws of transalkylation with changing molar ratios of phenol and 2,5-xylenol in feed mixtures were determined as follows:

Molar Ratio	**Mol fractions**				
(Phenol : 2,5-Xylenol)	Phenol	×	2,5-Xylenol	=	**Rate**
1:1	$\frac{1}{2}$	×	$\frac{1}{2}$	=	$\frac{1}{4}$
5:1	$\frac{5}{6}$	×	$\frac{1}{6}$	=	$\frac{5}{36} \approx \frac{1}{7}$
20:1	$\frac{20}{21}$	×	$\frac{1}{21}$	=	$\frac{20}{441} \approx \frac{1}{22}$

Mol fraction of 2,5-Xylenol	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{21}$
Relative mol fraction	1	$\frac{1}{3}$	$\approx \frac{1}{10}$
Rate	$\frac{1}{4}$	$\frac{1}{7}$	$\frac{1}{22}$
Relative rate	1	$\approx \frac{1}{2}$	$\approx \frac{1}{5}$

Appendix D: Calculation of the thermodynamic equilibrium carbon number distribution

A method of minimising the total Gibbs energy of compound mixtures for determining thermodynamic equilibria of complex chemical reaction systems, [van Ness and Abbot, 2001] was used for determining the carbon number distribution in thermodynamic equilibrium distribution for reactions carried out with different phenol : 2,5-xylenol ratios. In this method the following equations are solved simultaneously.

$$\frac{\Delta G_{fi}^{o}}{RT} + \ln \frac{n_i}{\sum_i n_i} + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0 \qquad \text{Equation D1}$$

$$\sum_i n_i a_{ik} = A_k \qquad \text{Equation D2}$$

Where: i determines a chemical species

ΔG_n° is the Gibbs free enthalpy of formation of the chemical species i

R is the gas constant

T is the temperature (in K)

n_i is the number of moles of species i

k identifies a particular atom

a_{ik} is the number of atoms of the k^{th} element present in each of the chemical species i

λ_k is a Lagrange multiplier for k

A_k is the total number of atomic masses of the k^{th} element in the feed

Equation D1 is based on the assumption that the activity or fugacity coefficients of all species i in the reaction mixture are all unity and therefore the equation is only applicable to an ideal gas phase or ideal solution. Because the studied

system was a solution of phenolic compounds in phenolic compounds, it could be assumed as being ideal and hence this equation could be applied

A computer programme [Möller, 2006] that models the system and solves the set of equations was used.

Appendix E: Chromatograms

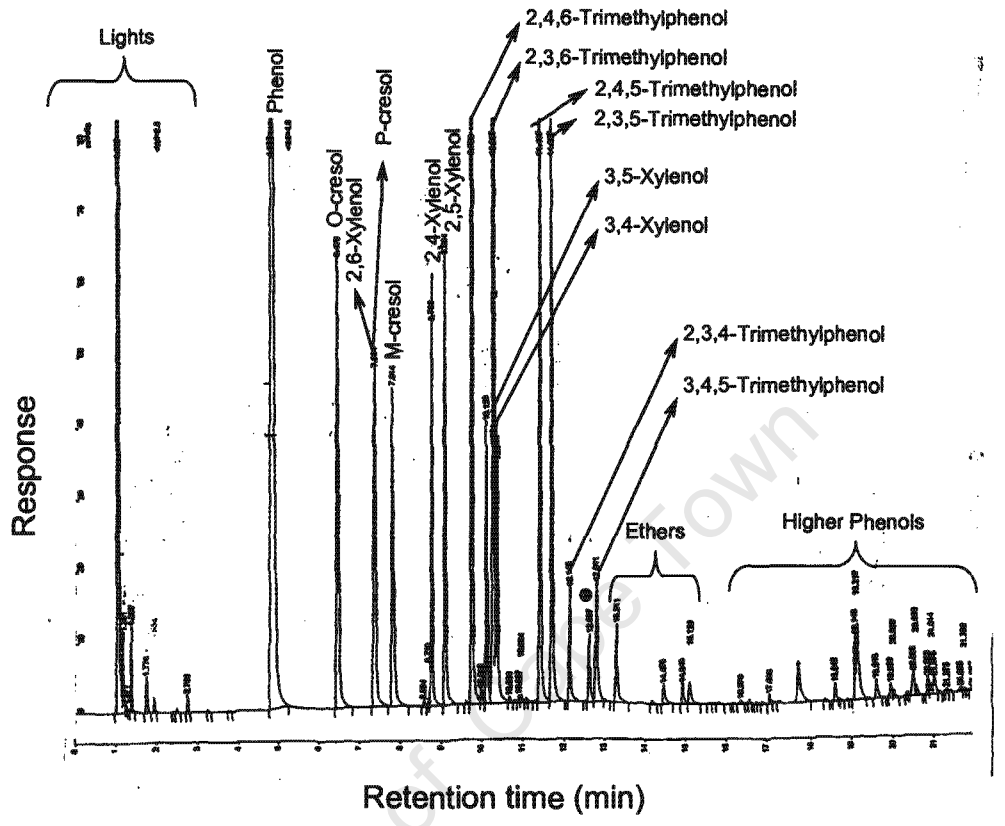

Figure E1: Product from 2,3,6-Trimethylphenol / phenol transalkylation (1 : 1 molar mixture)

Appendix E Chromatograms

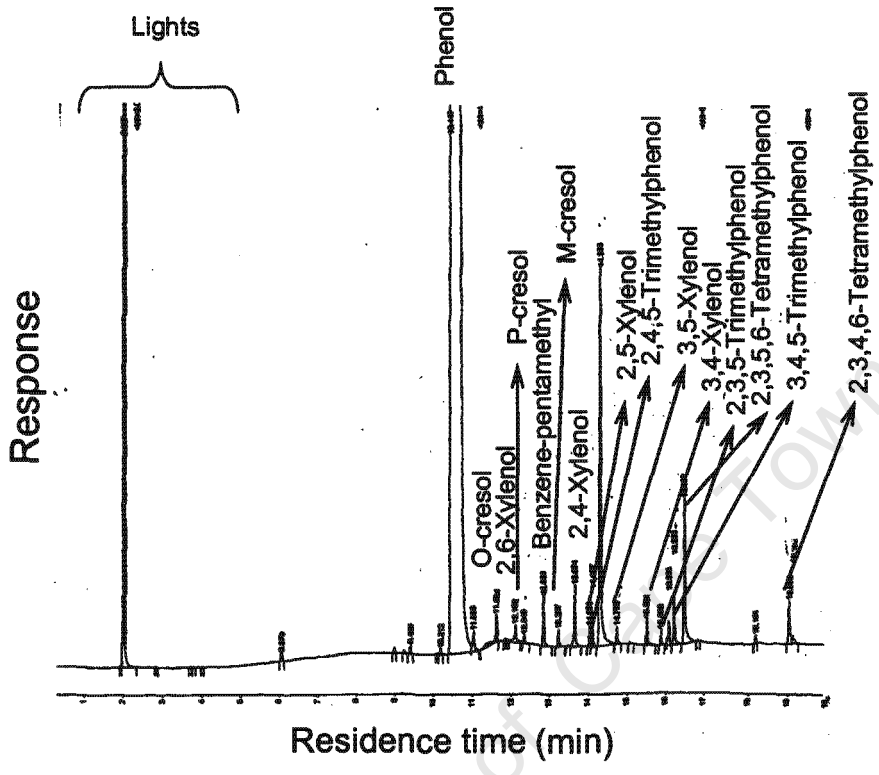

Figure E2: Simulated technical mixture with co-reactant phenol (1 : 20 molar mixture)

Appendix E Chromatograms

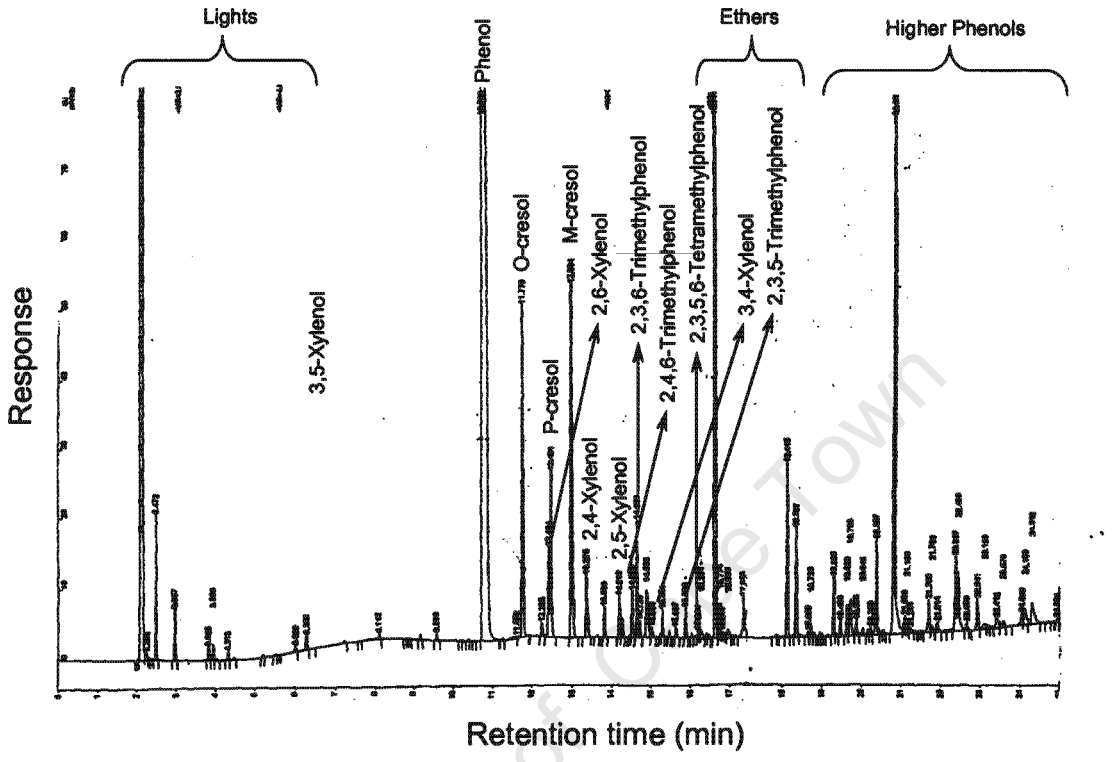

Figure E3: Product from simulated technical mixture / phenol transalkylation (1 : 20 molar mixture)

Appendix F: Summary of experimental results

Table F0: List of experiments that were carried out (in liquid phase at 60 bar, throughout) with mixtures of phenol and different co-feeds.

Exp	*Catalyst*	*Temperature (°C)*	*$WHSV_{total}$ (h^{-1})*	*Co-feed**	*Molar ratio***	*TOS*** (hrs)*
1	H-BEA-25	250 - 350	0.45	Xyl	1 : 1	319
2	H-BEA-25	400 - 450	0.45	Xyl	1 : 1	347
3	H-BEA-25	350	0.113 – 0.45	Xyl	1 : 1	299
4	H-MOR-90	350	0.113 – 0.45	Xyl	1 : 1	191
5	H-MFI-90	350	0.113 – 0.45	Xyl	1 : 1	249
6	H-MOR-90	350	0.113 – 0.45	Tmp	1 : 1	349
7	H-BEA-25	350	0.113 – 0.45	Xyl	5 : 1	566
8	H-BEA-25	350	0.113 – 0.45	Xyl	20 : 1	372
9	H-BEA-25	350	0.113 – 0.45	Tech	20 : 1	359
10	H-BEA-25	350	0.113	Xyl	1 : 1	226
11	H-BEA-25	350	0.225 – 0.90	****	-	112

*Xyl = 2,5-xylenol, Tmp = 2,3,6-trimethylphenol, Tech = simulated technical mixture

**Phenol : co-feed, molar ratio

***Time-on-stream

**** Feed was 2,5-xylenol in inert benzene solvent (in approximately 5 : 1 volume feed : solvent ratio)

Appendix F

Table F1: Results from experiment 1

Component (mole %)																				
Temperature (°C)	250	250	250	250	250	250	250	250	250	250	300	300	300	300	300	350	350	350	350	350
Sample	xt4(2.5)-1	xt4(2.5)-2	xt3(2.5)-3	xt4(2.5)-4	xt4(2.5)-5	xt4(2.5)-6	xt4(2.5)-7	xt4(2.5)-8	xt4(2.5)-9	xt4(2.5)-10	xt4(2.5)-11	xt4(2.5)-12	xt4(2.5)-13	xt4(2.5)-14	xt4(2.5)-15	xt4(2.5)-16	xt4(2.5)-17	xt4(2.5)-18	xt4(2.5)-19	xt4(2.5)-20
Time	16.4	22.36	43.04	47.51	62.75	76.9	92.2	114.4	136.7	142.9	159.3	167.6	182.4	190.2	206.9	214.4	221.4	228.12	246.8	253.9
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Toluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
p-xylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
o-xylene	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Other lights	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.4	0.5	0.6	0.5	0.5	1.0	1.1	0.4	0.2
Phenol	48.3	42.2	40.3	42.1	42.3	43.5	42.8	42.6	43.2	43.2	36.3	29.6	30.2	31.6	32.8	32.8	24.0	22.2	31.4	34.0
o-cresol	1.5	2.5	2.0	2.1	2.2	1.8	1.8	2.1	1.9	1.6	4.6	8.5	6.8	8.3	7.7	7.5	10.5	10.7	7.4	4.6
2,6-Xylenol	1.1	2.1	1.9	2.0	1.7	1.6	1.8	1.8	1.6	1.5	2.1	2.7	2.8	2.8	2.8	2.8	2.5	2.5	2.3	2.2
p-cresol	0.9	1.7	1.4	1.5	1.4	1.2	1.3	1.5	1.3	1.1	2.5	4.4	4.5	4.4	4.1	4.0	4.8	4.8	3.5	2.4
m-cresol	1.8	2.8	2.3	2.5	2.4	2.0	2.1	2.4	2.2	2.0	4.8	8.5	6.7	8.3	7.7	7.8	11.4	11.6	8.0	5.2
2,4-Xylenol	5.3	11.5	11.3	12.1	11.0	10.9	11.8	11.4	10.9	10.5	9.0	7.5	7.5	8.1	8.5	8.5	5.7	5.1	6.1	7.2
2,5-Xylenol	29.2	25.8	25.7	26.9	28.9	30.4	29.0	28.2	30.1	31.5	22.7	13.5	13.1	14.3	15.3	15.4	8.6	7.4	18.4	25.2
2,4,6-trimethylphenol	0.3	0.2	1.4	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.4	0.6	0.7	0.6	0.5	0.5	0.7	0.7	0.5	0.4
2,3-Xylenol	1.0	1.8	1.9	1.8	1.4	1.3	1.5	1.5	1.2	1.2	1.7	2.1	2.2	2.2	2.4	2.4	2.0	2.4	1.7	1.5
2,3,6-trimethylphenol	0.7	1.3	1.4	1.3	1.0	0.9	1.1	1.0	0.9	0.9	1.2	1.6	1.6	1.6	1.4	1.4	1.4	0.9	1.3	1.1
3,5-Xylenol	0.6	0.7	0.9	0.7	0.3	0.6	0.6	0.7	0.6	0.9	1.0	1.4	1.4	1.4	1.3	1.3	1.7	1.7	1.4	1.1
3,4-Xylenol	1.1	2.2	1.8	1.9	1.6	1.4	1.7	1.6	1.4	1.3	2.5	3.5	3.6	3.5	3.4	3.4	4.2	4.3	3.5	2.9
2,3,5-trimethylphenol	0.2	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.5	0.8	0.9	0.8	0.8	0.7	0.8	0.8	0.7	0.5
3,4,5-trimethylphenol	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.5	0.8	0.8	0.8	0.7	0.7	0.9	0.9	0.6	0.4
diphenylether	1.1	2.3	2.1	2.2	2.0	1.8	2.1	2.1	1.9	1.8	2.3	2.6	2.6	2.6	2.6	2.6	2.7	2.8	2.6	2.4
3-phenoxytoluene	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.8	0.7	0.7	0.7	0.7	1.3	1.6	1.2	0.8
4-phenoxytoluene	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.7	0.6	0.6	0.6	0.6	0.9	1.0	0.8	0.5
Unknown	0.3	0.6	0.5	0.6	0.6	0.5	0.5	0.6	0.6	0.5	0.9	1.4	1.4	1.4	1.3	1.2	1.6	1.6	1.2	0.9
Unknown	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.7	0.7	0.6	0.5	0.5	1.1	1.1	0.7	0.4
Higher phenols	6.0	1.2	3.9	1.0	1.6	0.6	0.8	0.9	1.0	0.9	5.5	7.7	6.4	4.9	4.3	4.7	11.9	14.7	6.1	6.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2,5 conversion	41.5	48.5	48.6	46.2	42.2	39.1	42.1	43.6	39.8	37.0	54.5	73.0	73.9	71.3	69.4	69.2	82.7	85.2	63.2	49.6
Phenol conversion	3.4	15.6	19.3	15.8	15.4	13.0	14.4	14.5	13.5	13.5	27.5	40.4	39.6	36.9	34.4	34.3	52.0	55.6	37.1	31.9
Total conversion	22.5	32.1	34.0	31.0	28.8	26.1	28.3	29.0	26.7	25.3	41.0	56.7	56.7	54.1	51.9	51.8	67.4	70.4	50.2	40.8
Ave Time	8.2	3.0	10.3	2.2	7.6	4.1	10.7	11.1	11.2	3.1	8.2	4.1	7.4	3.9	8.4	3.8	3.5	3.4	9.3	3.8
TOS (hrs)	8.2	19.4	32.7	45.3	55.1	66.6	81.6	103.3	125.6	139.8	151.1	163.5	175.0	186.3	198.6	210.7	217.9	224.8	237.5	250.4

Table F1 (continued)

Component (mole %)						
Temperature (oC)	350	350	350	350	350	300
Sample	xt4(2.5)-21	xt4(2.5)-22	xt4(2.5)-23	xt4(2.5)-24	xt4(2.5)-25	xt4(2.5)-26
Time	269.1	276.2	283.2	300.2	316.9	322
Benzene	0.0	0.0	0.0	0.0	0.0	0.0
Toluene	0.0	0.0	0.0	0.0	0.0	0.0
p-xylene	0.0	0.0	0.0	0.0	0.0	0.0
o-xylene	0.2	0.1	0.1	0.1	0.1	0.0
Other lights	0.6	0.6	0.7	0.8	0.4	0.6
Phenol	30.0	26.8	25.7	26.3	28.2	30.3
o-cresol	8.0	9.0	9.0	8.9	8.0	8.0
2,6-Xylenol	2.8	2.9	2.8	2.8	2.9	3.1
p-cresol	3.9	4.3	4.3	4.2	3.8	3.9
m-cresol	8.5	9.4	9.4	9.2	8.1	8.2
2,4-Xylenol	7.2	6.6	6.4	6.5	6.9	7.7
2,5-Xylenol	13.3	10.3	9.8	10.0	10.9	12.3
2,4,6-trimethylphenol	0.5	0.6	0.6	0.6	0.5	0.5
2,3-Xylenol	2.1	1.8	1.6	1.8	1.8	1.9
2,3,6-trimethylphenol	1.5	1.3	1.3	1.3	1.3	1.4
3,5-Xylenol	1.6	1.7	1.6	1.6	1.5	1.6
3,4-Xylenol	4.0	4.3	4.2	4.1	3.9	4.1
2,3,5-trimethylphenol	0.7	0.7	0.8	0.7	0.7	0.7
3,4,5-trimethylphenol	0.7	0.8	0.8	0.7	0.6	0.7
diphenylether	3.1	3.3	3.6	3.5	3.7	4.1
3-phenoxytoluene	1.2	1.3	1.5	1.5	1.2	1.3
4-phenoxytoluene	0.8	0.9	1.0	1.0	0.9	0.9
Unknown	1.3	1.4	1.6	1.5	1.4	1.3
Unknown	0.6	0.7	0.7	0.7	1.0	0.7
Higher phenols	7.4	11.1	12.4	12.5	12.4	8.5
Total	100.0	100.0	100.0	100.0	100.0	100.0
2,5 conversion	73.4	78.5	80.3	78.9	76.2	75.4
Phenol conversion	39.9	46.4	48.7	47.5	43.6	39.4
Total conversion	56.7	62.9	64.5	63.7	60.9	57.4
Ave Time	7.6	3.5	8.5	3.5	6.3	2.6
TOS (hrs)	261.5	272.7	284.7	298.7	306.6	319.5

Appendix F

Table F2: Results from experiment 2

Component (mole %)																		
Temperature (°C)	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	450	450
Sample	xt3(2.5)-1	xt3(2.5)-2	xt3(2.5)-3	xt3(2.5)-4	xt3(2.5)-5	xt3(2.5)-6	xt3(2.5)-7	xt3(2.5)-8	xt3(2.5)-9	xt3(2.5)-10	xt3(2.5)-11	xt3(2.5)-12	xt3(2.5)-13	xt3(2.5)-14	xt3(2.5)-15	xt3(2.5)-16	xt3(2.5)-17	xt3(2.5)-18
Time	22.28	27.45	43.46	51.53	71.73	96.3	115.73	123.27	142.81	147.33	163.81	171.65	187.35	195.58	211.61	219.83	240	262.66
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Toluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
p-xylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
o-xylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Other lights	3.9	2.7	2.3	1.5	1.6	1.6	0.8	1.1	1.8	1.1	0.9	0.9	0.8	0.7	0.8	0.9	1.4	0.8
Phenol	20.1	26.0	21.4	25.8	22.8	24.2	32.1	23.8	25.0	28.2	27.2	27.2	27.7	27.2	26.7	27.1	25.8	28.4
o-cresol	10.0	9.6	12.3	9.2	12.9	11.3	7.3	12.2	12.9	10.4	9.8	9.4	9.7	9.6	9.2	8.6	10.0	6.9
2,6 Xylenol	1.4	1.3	1.6	1.5	1.9	1.9	1.6	1.8	1.9	1.8	1.7	1.7	1.7	1.6	1.6	1.2	1.1	0.9
p-cresol	3.6	3.6	4.7	3.6	5.0	4.6	3.2	4.9	5.3	4.7	4.5	4.4	4.5	4.4	4.2	3.4	3.5	2.0
m-cresol	10.0	9.6	12.3	9.2	12.9	11.3	7.3	12.2	12.9	10.4	9.8	9.4	9.7	9.6	9.2	8.6	10.0	6.9
2,4 Xylenol	8.1	11.9	6.4	11.4	7.7	9.8	15.6	9.5	8.2	10.2	10.4	10.6	11.5	11.5	11.5	13.3	11.0	16.7
2,5 Xylenol	8.1	11.9	6.4	11.4	7.7	9.6	15.6	9.5	8.2	10.2	10.4	10.6	11.5	11.5	11.5	13.3	11.0	16.7
2,4,6-trimethylphenol	0.1	0.2	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3
2,3 Xylenol	1.9	1.6	2.2	2.0	2.6	2.5	2.0	2.5	2.6	2.4	2.4	2.3	2.3	2.2	2.2	1.9	1.8	0.3
2,3,6-trimethylphenol	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.3
3,4-Xylenol	1.8	1.5	2.0	1.5	2.3	2.0	1.2	1.9	2.0	1.5	1.5	1.4	1.4	1.4	1.3	1.2	1.1	0.8
3,5-Xylenol	1.8	1.5	2.0	1.7	2.1	2.0	1.4	2.0	2.1	1.8	1.8	1.7	1.7	1.7	0.9	1.5	1.5	1.2
2,3,5-trimethylphenol	0.6	0.5	0.6	0.7	0.8	0.9	0.7	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	1.0	0.6
3,4,5-trimethylphenol	0.5	0.4	0.6	0.7	0.7	0.6	0.8	0.8	0.8	1.1	1.1	1.1	1.1	1.1	1.1	1.0	0.6	0.9
diphenylether	1.7	1.1	1.4	1.1	1.7	1.8	1.1	1.5	1.7	1.7	1.5	1.0	1.4	1.4	1.5	0.9	0.5	0.2
3-phenoxytoluene	1.8	1.0	1.3	0.8	1.4	0.9	0.3	0.9	0.8	0.4	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.0
4-phenoxytoluene	1.0	0.7	1.0	0.8	0.8	0.6	0.4	0.6	0.6	0.4	0.3	0.3	0.3	0.3	0.3	0.5	0.1	0.0
Unknown	1.6	1.1	1.4	1.0	1.2	1.0	0.7	0.9	0.9	0.9	0.9	1.0	0.9	0.9	1.0	0.9	0.8	0.5
Unknown	1.3	1.1	1.9	1.5	0.8	0.7	0.5	0.7	0.6	1.0	1.1	1.1	0.6	0.8	0.8	1.1	1.1	0.8
Higher phenols	20.5	12.3	17.5	14.3	12.7	12.8	7.1	11.9	10.3	10.5	12.9	14.4	11.7	12.5	14.3	13.1	16.8	14.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2,5 conversion	83.9	76.2	87.1	77.3	84.6	80.8	68.9	81.0	83.5	79.6	79.2	78.8	77.0	77.0	76.9	73.3	77.9	66.5
Phenol conversion	59.9	47.9	57.3	48.4	54.3	51.6	35.8	52.3	49.9	43.6	45.5	45.7	44.7	45.6	46.5	45.9	46.8	43.2
Total	71.9	62.1	72.2	62.8	69.4	66.2	52.3	66.7	66.7	61.6	62.3	62.3	60.8	61.3	61.7	59.6	63.4	54.9
Ave Time	11.1	2.8	8.0	4.0	10.1	12.3	9.7	3.8	9.7	2.4	8.2	3.9	7.8	4.0	8.1	4.1	14.6	6.9
TOS (hrs)	11.1	24.9	35.5	47.5	61.8	84.0	100.0	119.5	132.9	145.0	155.6	167.7	179.5	191.4	203.5	215.7	234.4	255.9

Table F2 (continued)

Component (mole %)							
Temperature (oC)	450	400	400	400	450	400	450
Sample	xt3(2.5)-19	xt3(2.5)-20	xt3(2.5)-21	xt3(2.5)-22	xt3(2.5)-23	xt3(2.5)-24	xt3(2.5)-25
Time	284.68	290.9	308.86	325.31	332.15	338.6	355.76
Benzene	0.0	0.1	0.1	0.1	0.1	0.1	0.1
Toluene	0.0	0.2	0.2	0.1	0.1	0.1	0.1
p-xylene	0.0	0.1	0.2	0.1	0.1	0.1	0.1
o-xylene	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Other lights	0.6	0.1	0.1	0.1	0.1	0.1	0.1
Phenol	26.6	25.2	25.4	24.8	25.1	25.1	25.6
o-cresol	5.9	6.5	6.6	6.2	4.9	4.6	4.7
2,6 Xylenol	0.6	0.6	0.5	0.5	0.3	0.3	0.3
p-cresol	1.2	1.1	1.0	0.6	0.6	0.6	0.5
m-cresol	5.9	6.5	6.6	6.2	4.9	4.6	4.7
2,4 Xylenol	19.7	23.5	24.1	25.2	26.8	27.8	26.7
2,5 Xylenol	19.7	23.5	24.1	25.2	26.6	27.8	26.7
2,4,6-trimethylphenol	0.3	0.2	0.2	0.2	0.2	0.2	0.2
2,3 Xylenol	1.4	0.6	0.8	0.9	0.6	0.6	0.4
2,3,6-trimethylphenol	0.3	0.0	0.0	0.0	0.0	0.0	0.0
3,4-Xylenol	0.5	0.5	0.6	0.8	0.5	0.6	0.6
3,5-Xylenol	0.9	0.7	0.6	0.7	0.7	0.5	0.5
2,3,5-trimethylphenol	0.6	0.1	0.1	0.2	0.2	0.0	0.2
3,4,5-trimethylphenol	0.7	0.2	0.2	0.3	0.2	0.1	0.2
diphenylether	0.2	0.0	0.0	0.0	0.0	0.0	0.0
3-phenoxytoluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4-phenoxytoluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	0.4	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	0.6	0.0	0.0	0.0	0.0	0.0	0.0
Higher phenols	11.5	9.9	8.6	7.8	7.5	8.7	8.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2,5 conversion	60.6	53.1	51.8	48.6	48.3	44.3	46.7
Phenol conversion	42.4	49.5	49.2	50.5	49.8	49.8	48.8
Total	51.5	51.3	50.5	50.0	48.0	47.1	47.7
Ave Time	10.9	3.1	9.0	8.2	3.4	3.7	8.1
TOS (hrs)	273.8	287.8	299.9	317.1	328.7	335.9	347.7

Appendix F

Table F3: Results from experiment 3

Component (Mole%)																
Sample	xt9-1	xt9-2	xt9-3	xt9-4	xt9-5	xt9-6	xt9-7	xt9-8	xt9-9	xt9-10	xt9-11	xt9-12	xt9-13	xt9-14	xt9-15	xt9-16
Time (hrs)	19.98	42.76	67.15	90.8	115.91	125.28	162.61	170.18	192.02	199.15	209.86	216.75	235.91	262.01	282.46	315.58
Pump Rate	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.01	0.01	0.01	0.01
Cyclohexane	0.00	0.55	1.17	1.05	0.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.47
Benzene	0.48	1.33	1.85	1.70	0.95	0.68	0.50	0.43	0.40	0.45	0.29	0.28	0.22	0.38	0.56	0.75
Toluene	0.53	2.71	2.76	2.41	1.03	0.59	0.45	0.43	0.44	0.37	0.19	0.23	0.22	0.47	0.84	0.95
p-xylene	0.29	1.45	1.33	1.12	0.50	0.28	0.24	0.23	0.25	0.18	0.10	0.12	0.12	0.31	0.48	0.50
o-xylene	0.09	0.44	0.39	0.34	0.15	0.08	0.08	0.07	0.08	0.00	0.00	0.00	0.04	0.10	0.18	0.15
Other Lights	0.07	1.00	0.70	0.49	0.15	0.03	0.08	0.05	0.04	0.07	0.07	0.04	0.03	0.08	0.22	0.12
Phenol	33.37	21.98	19.76	18.60	22.62	25.05	24.20	24.83	26.18	31.57	33.83	31.85	31.42	25.77	25.17	27.55
o-cresol	7.82	11.73	11.76	11.49	12.00	12.35	12.04	11.88	11.56	6.45	7.33	8.22	8.04	12.18	12.27	11.75
2,6 Xylenol	1.78	1.90	1.95	1.89	2.27	3.49	3.37	3.37	3.34	2.04	2.09	2.13	2.09	2.28	2.20	2.23
p-cresol	4.24	4.67	4.55	4.42	5.30	4.49	4.38	4.38	4.34	5.41	5.37	5.46	5.35	5.57	5.38	5.47
m-cresol	9.03	13.75	13.87	13.36	13.46	13.50	13.23	13.07	12.74	9.40	8.19	9.04	8.89	13.46	14.48	14.34
2,4 Xylenol	6.87	3.65	3.46	3.38	4.72	5.25	5.26	5.39	5.67	7.73	8.52	7.84	7.76	5.03	4.59	4.93
2,5 Xylenol	18.05	5.66	4.87	4.40	6.37	7.24	7.19	7.38	8.09	12.11	13.08	12.05	11.76	7.29	7.26	6.67
2,4,6-trimethylphenol	2.56	1.94	1.99	1.93	2.79	3.17	3.18	3.22	3.17	3.52	3.87	3.76	3.70	2.79	2.38	2.33
2,3-Xylenol	3.15	2.92	2.92	2.92	4.00	4.45	4.57	4.62	4.40	3.79	4.35	4.33	5.41	3.79	3.18	2.85
2,3,6 trimethylphenol	0.53	0.44	0.46	0.44	0.59	0.62	0.62	0.60	0.58	0.48	0.43	0.47	0.46	0.56	0.55	0.55
3,5-Xylenol	2.03	1.90	1.92	1.86	2.50	2.76	2.68	2.95	2.81	2.61	2.99	2.94	2.99	2.35	2.12	2.00
2,3,5-trimethylphenol	0.80	0.47	0.47	0.49	0.71	0.77	0.79	0.77	0.74	0.75	0.57	0.70	0.59	0.72	0.70	0.71
2,3,4-trimethylphenol	0.84	0.56	0.62	0.84	0.79	0.85	0.68	0.86	0.80	0.70	0.62	0.73	0.68	0.79	0.73	0.72
3,4,5-trimethylphenol	0.13	0.18	0.17	0.16	0.15	0.16	0.17	0.18	0.15	0.10	0.09	0.09	0.11	0.18	0.16	0.14
diphenylether	1.25	1.35	1.80	1.69	2.62	3.12	3.41	3.40	3.10	2.70	2.99	3.39	3.42	3.28	2.36	1.93
3-phenoxytoluene	0.82	1.28	1.94	2.24	1.84	1.45	1.57	1.51	1.42	1.11	0.71	0.94	0.94	1.97	2.22	1.86
4-phenoxytoluene	0.44	0.73	1.03	1.18	1.08	1.00	1.08	1.10	1.01	0.70	0.56	0.73	0.70	1.24	1.21	0.98
Unknown	0.81	1.02	1.52	1.98	1.85	1.82	2.03	1.94	1.72	1.27	1.22	1.38	1.30	1.56	1.29	1.07
Unknown	0.46	0.70	1.14	1.44	1.08	0.69	0.94	0.86	0.71	0.59	0.34	0.48	0.38	0.74	0.72	0.85
Higher Phenols	4.13	15.70	15.98	18.17	9.76	5.83	6.93	6.49	6.29	3.90	2.17	2.97	3.36	7.08	8.42	6.32
Total	100.00	100.00	100.00	108.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.08	100.00	100.00	100.00
2,5 conversion	63.90	88.68	90.65	91.19	87.26	85.53	85.62	85.22	83.82	75.78	73.69	75.90	76.48	85.41	85.47	82.85
Phenol conversion	33.26	56.08	60.47	62.80	54.75	49.91	51.60	50.34	47.85	38.86	32.34	36.70	37.17	48.46	49.65	44.89
Total conversion	48.58	72.38	75.56	77.00	71.01	67.72	68.61	67.78	65.73	58.32	53.11	56.30	56.82	66.94	67.56	63.77
Ave Time	9.99	11.39	12.195	11.825	12.555	4.685	18.665	3.785	10.92	3.565	5.355	3.445	9.58	13.05	10.225	16.56
TOS (hrs)	9.99	31.37	54.96	78.96	103.36	120.60	143.96	166.40	181.10	195.59	204.51	213.31	228.33	248.96	272.24	299.02

Table F4: Results from experiment 4

Component (Mole%)												
Sample	xt7-1	xt7-2	xt7-3	xt7-4	xt7-5	xt7-6	xt7-7	xt7-8	xt7-9	xt7-10	xt7-11	xt7-12
Time (hrs)	21.86	46.00	70.00	96.04	116.00	124.70	139.36	148.90	163.73	171.00	187.85	194.60
Pump Rate	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04
Benzene	0.33	0.38	0.37	0.31	0.33	0.24	0.23	0.19	0.19	0.18	0.18	0.21
Toluene	0.40	0.43	0.34	0.25	0.14	0.13	0.13	0.12	0.10	0.08	0.07	0.07
p-xylene	0.23	0.21	0.17	0.14	0.08	0.05	0.05	0.05	0.03	0.03	0.08	0.00
o-xylene	0.07	0.07	0.05	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
Other Lights	0.04	0.04	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	30.01	34.33	38.28	37.40	39.67	38.37	38.71	38.96	42.69	43.59	42.93	44.58
o-cresol	9.24	8.69	8.14	7.46	3.61	2.63	2.84	2.83	1.94	1.86	1.67	1.35
2,6 Xylenol	2.07	1.97	1.86	1.75	1.42	1.58	1.58	1.54	1.33	1.35	1.52	1.37
p-cresol	4.62	4.50	4.15	3.92	3.18	3.72	3.53	3.46	2.99	3.03	3.41	3.07
m-cresol	12.03	11.80	11.17	10.46	5.12	3.29	3.26	3.24	2.31	2.08	2.01	1.71
2,4 Xylenol	6.26	5.74	5.06	5.86	8.38	10.14	10.13	9.95	10.16	10.91	11.99	11.91
2,5 Xylenol	15.22	16.59	18.61	20.46	24.16	21.51	21.68	21.85	25.58	25.07	21.97	24.15
2,3 Xylenol	2.95	2.33	2.25	2.13	2.77	3.74	3.69	3.54	2.99	3.11	3.85	3.24
Phenol, 3-ethyl	0.30	0.16	0.12	0.08	0.08	0.08	0.09	0.14	0.08	0.08	0.07	0.07
2,3,6-trimethylphenol	0.06	0.36	0.37	0.36	0.00	0.08	0.00	0.08	0.00	0.00	0.00	0.00
3,4-Xylenol	3.87	2.51	2.24	2.01	2.69	3.78	3.70	3.55	2.68	2.54	2.87	2.42
3,5-Xylenol	2.53	1.78	1.66	1.52	1.70	2.40	2.36	2.36	1.84	1.78	2.04	1.67
2,3,5-trimethylphenol	1.08	0.97	0.85	0.67	0.38	0.17	0.15	0.23	0.08	0.07	0.19	0.08
3,4,5-trimethylphenol	0.90	0.62	0.58	0.56	0.30	0.14	0.12	0.19	0.08	0.07	0.08	0.08
diphenylether	1.95	1.49	1.38	1.16	2.26	4.56	4.54	4.15	3.01	2.86	3.27	2.73
3-phenoxytoluene	1.00	0.69	0.57	0.46	0.36	0.45	0.43	0.39	0.19	0.12	0.10	0.07
4-phenoxytoluene	0.62	0.46	0.38	0.32	0.26	0.36	0.35	0.33	0.17	0.12	0.08	0.07
Hydroquinone	0.00	0.00	0.08	0.00	0.08	0.16	0.17	0.15	0.02	0.03	0.08	0.04
Unknown	0.72	0.64	0.67	0.69	0.97	0.96	0.92	0.84	0.57	0.48	0.50	0.40
Unknown	0.38	0.35	0.36	0.35	0.33	0.12	0.11	0.19	0.05	0.03	0.03	0.08
Higher Phenols	3.21	2.52	1.61	1.38	1.47	1.22	1.25	1.73	0.94	0.08	1.12	0.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.08	108.00	100.00	100.08	100.08	108.00
2,5 conversion	66.6	66.8	62.8	59.1	51.6	57.0	56.6	56.3	48.9	49.9	58.1	51.7
Phenol conversion	40.0	31.3	27.4	25.2	20.7	23.3	22.6	22.1	14.6	12.8	14.1	10.8
Total conversion	54.8	49.1	45.1	42.1	38.1	40.1	39.6	39.2	31.8	31.3	35.1	31.3
Ave Time	10.78	12.22	12	13.02	9.98	4.35	7.33	3.72	8.465	3.835	8.325	3.475
TOS (hrs)	10.78	33.78	58	83.62	106.62	120.35	132.03	143.06	155.265	167.365	179.325	191.125

Appendix F

Table F5: Results from experiment 5

Component (Mole%)																
Sample	xt5-1	xt5-2	xt5-3	xt5-4	xt5-5	xt5-6	xt5-7	xt5-8	xt5-9	xt5-10	xt5-11	xt5-12	xt5-13	xt5-14	xt5-15	xt5-16
Time (hrs)	26.41	50.11	72.88	96.46	118.26	122.35	139.71	146.43	162.73	169.5	186.76	193.93	210.41	216.26	237.1	282.16
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.04	0.04
Benzene	0.70	0.86	1.17	1.24	0.78	0.69	0.42	0.32	0.27	0.26	0.18	0.20	0.17	0.26	0.15	0.12
Toluene	2.26	2.96	3.42	3.40	2.61	2.27	1.35	1.12	1.02	0.96	0.58	0.46	0.44	0.90	0.48	0.36
p-xylene	1.49	1.94	2.35	2.19	1.72	1.46	0.86	0.50	0.41	0.36	0.16	0.12	0.11	0.44	0.16	0.09
o-xylene	0.40	0.52	0.82	0.58	0.47	0.40	0.19	0.15	0.12	0.11	0.05	0.04	0.03	0.13	0.05	0.03
Other Lights	0.99	1.26	2.14	1.41	1.07	0.82	0.18	0.13	0.09	0.08	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	32.60	22.44	16.19	15.71	17.20	18.83	31.19	31.85	31.74	34.68	40.79	42.78	42.93	33.00	41.94	43.88
o-cresol	4.19	7.63	8.48	9.42	9.55	9.21	6.20	5.95	5.09	4.73	2.83	1.93	1.95	4.79	2.20	1.42
2,6 Xylenol	0.60	1.26	1.26	1.42	1.50	1.54	1.56	1.69	1.81	2.08	1.82	1.78	1.84	1.60	1.79	1.89
p-cresol	2.36	3.73	3.75	4.20	4.45	4.56	4.61	5.00	4.68	4.35	3.69	3.81	3.94	3.85	3.84	3.83
m-cresol	5.44	9.84	10.70	11.90	12.07	11.73	8.11	7.83	6.86	8.19	3.46	2.52	2.57	6.24	2.94	1.89
2,4 Xylenol	5.17	4.40	2.82	3.26	3.65	4.22	7.77	7.96	7.89	8.81	11.21	11.75	11.70	8.68	11.76	12.27
2,5 Xylenol	20.59	9.71	4.33	4.70	5.12	5.83	11.14	10.91	10.69	11.98	15.56	16.47	16.34	12.14	16.34	17.73
2,4,6-trimethylphenol	0.23	0.37	0.41	0.44	0.41	0.35	0.22	0.19	0.15	0.13	0.07	0.05	0.05	0.13	0.05	0.03
2,3 Xylenol	1.46	2.15	1.99	2.40	2.73	2.97	3.50	4.07	3.85	3.91	3.03	2.88	3.08	2.60	2.81	2.58
Phenol, 3-ethyl	1.02	1.84	1.84	1.95	1.84	1.67	0.98	0.68	0.71	0.83	0.34	0.24	0.24	0.60	0.30	0.20
2,3,6-trimethylphenol	0.25	0.42	2.65	0.52	0.51	0.54	0.46	0.50	0.36	0.42	0.25	0.18	0.18	0.31	0.21	0.14
3,5 Xylenol	2.05	2.65	2.11	3.32	3.27	2.93	2.22	2.35	2.14	1.97	1.26	1.12	1.19	1.69	1.05	0.92
3,4 Xylenol	3.04	2.97	0.88	2.44	2.68	2.98	4.95	0.52	5.12	5.70	7.05	7.43	7.43	5.50	7.37	7.69
2,3,5-trimethylphenol	0.40	0.82	0.37	0.71	0.81	0.84	0.60	0.91	0.79	0.77	0.49	0.38	0.39	0.83	0.43	0.36
3,4,5-trimethylphenol	0.48	0.59	0.72	0.79	0.77	0.67	0.41	0.42	0.32	0.30	0.17	0.11	0.12	0.33	0.15	0.21
diphenylether	2.19	2.43	3.53	3.84	3.83	3.53	2.70	3.49	3.14	3.13	2.10	1.92	2.00	3.01	1.83	1.80
3-phenoxytoluene	1.86	3.13	4.29	4.18	4.03	4.01	2.31	2.28	1.84	1.72	0.86	0.58	0.57	2.69	0.72	0.39
4-phenoxytoluene	0.82	0.97	1.47	1.26	1.12	1.03	0.49	0.44	0.36	0.37	0.17	0.13	0.69	0.47	0.15	0.08
Hydroquinone	0.22	0.47	0.68	0.68	0.73	0.67	0.57	0.70	0.83	0.85	0.51	0.49	0.52	0.68	0.45	0.45
Unknown	1.53	2.31	3.23	3.24	2.98	2.78	1.70	1.70	1.47	1.35	0.83	0.83	0.59	1.44	0.84	0.44
Unknown	1.31	1.37	2.03	0.53	1.42	1.38	0.53	0.39	0.51	0.25	0.10	0.12	0.05	0.71	0.08	0.04
Higher Phenols	6.39	11.25	16.78	14.29	12.73	12.69	4.77	7.77	6.30	4.16	2.37	1.91	1.46	7.40	2.13	1.77
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2,6 conversion	58.6	80.6	91.3	90.6	89.6	88.3	77.7	76.2	76.6	76.1	68.9	67.1	67.3	75.7	67.3	64.5
Phenol conversion	34.8	55.1	67.6	68.6	65.6	62.3	37.6	36.3	36.5	30.6	18.4	14.5	14.1	34.0	18.1	12.2
Total conversion	46.6	67.9	79.5	79.6	77.7	75.3	57.7	57.2	57.6	53.4	43.7	40.8	40.7	54.9	41.7	38.4
Ave Time	13.205	16.35	6.885	11.79	9.9	3.045	8.68	3.36	8.15	3.385	8.63	3.585	8.24	2.925	10.42	12.54
TOS (hrs)	13.205	42.78	65.995	84.67	108.36	119.305	131.03	143.07	154.58	166.115	178.13	190.345	202.17	213.335	226.66	249.84

Table F6: Results from experiment 6

Component (Mole%)																			
Sample	xt6-1	xt6-2	xt6-3	xt6-4	xt6-5	xt6-6	xt6-7	xt6-8	xt6-9	xt6-10	xt6-11	xt6-12	xt6-13	xt6-14	xt6-15	xt6-16	xt6-17	xt6-18	xt6-19
Time (hrs)	17.85	41.95	65.55	88.16	114.18	138.21	145.86	162.55	169.8	186.68	193.64	210.61	213.53	230.9	254.56	280.28	314.8	337.6	361.53
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.01	0.01	0.01	0.01	0.01
Benzene	0.48	0.50	0.47	0.37	0.40	0.54	0.38	0.23	0.27	0.15	0.10	0.12	0.25	0.17	0.13	0.20	0.25	0.27	0.33
Toluene	0.55	0.80	0.38	0.26	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.10	0.11	0.15	0.19
p-xylene	0.51	0.41	0.24	0.17	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.13	0.13	0.16	0.18
o-xylene	0.18	0.14	0.09	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.08	0.08	0.07	0.07
Other Lights	0.35	0.28	0.17	0.14	0.09	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.03	0.03	0.03	0.08	0.04	0.05
Phenol	18.05	23.70	27.42	29.17	29.76	39.64	43.65	41.87	42.68	41.76	43.67	43.08	43.48	43.18	40.12	29.69	27.83	26.37	26.05
o-cresol	5.98	6.62	6.40	6.15	5.95	3.30	2.06	2.01	2.09	2.20	1.70	1.15	0.97	1.09	1.57	3.79	4.54	5.42	5.61
2,6 Xylenol	1.47	1.74	1.66	1.59	1.53	0.68	0.58	0.61	0.76	0.60	0.62	0.41	0.36	0.38	0.39	0.87	1.03	1.21	1.34
p-cresol	3.59	4.27	4.07	3.90	3.75	2.17	1.42	1.31	1.17	1.22	1.13	0.63	0.55	0.57	0.96	2.14	2.52	2.97	3.26
m-cresol	5.93	5.48	4.78	4.38	4.14	1.60	0.84	0.86	0.92	0.97	0.67	0.44	0.44	0.50	0.80	2.55	3.17	3.97	4.39
2,4 Xylenol	3.69	4.21	3.80	3.55	3.38	1.89	0.96	1.02	1.03	1.09	0.60	0.59	0.54	0.59	0.85	2.09	2.57	3.15	3.38
2,5 Xylenol	5.09	5.31	4.72	4.39	4.20	2.17	1.29	1.30	1.31	1.37	1.02	0.73	0.65	0.70	0.89	2.55	3.15	3.91	4.21
2,4,6-trimethylphenol	7.81	8.22	8.93	8.11	9.41	9.47	9.88	10.22	10.11	10.27	9.34	11.09	11.95	11.68	11.07	9.51	9.58	9.43	9.40
2,3-Xylenol	3.78	3.10	2.81	2.65	2.58	1.12	0.58	0.64	0.68	0.72	0.50	0.38	0.39	0.45	0.75	2.28	2.67	3.07	3.17
2,3,6 trimethylphenol	7.84	11.48	12.49	12.80	13.10	21.59	23.65	22.71	21.65	21.08	25.02	19.13	13.37	12.71	9.97	7.50	6.14	9.04	9.76
3,5-Xylenol	3.01	2.84	2.72	2.54	2.58	1.89	1.41	1.29	1.35	1.08	1.22	0.94	0.80	0.96	1.10	2.29	2.45	2.83	2.88
2,3,5-trimethylphenol	5.93	4.28	4.63	4.77	4.97	4.71	5.02	5.72	5.87	6.00	5.21	7.65	9.38	9.48	10.11	9.07	7.98	6.76	6.18
3,4,5-trimethylphenol	6.88	4.47	4.90	5.04	5.31	4.73	4.97	5.79	5.79	6.09	5.34	8.10	9.96	10.15	11.28	10.39	8.91	7.44	6.72
2,3,5,6-tetramethylphenol	2.02	1.14	1.58	1.53	1.58	1.08	0.68	1.00	0.97	1.01	0.91	1.29	1.53	1.55	2.04	2.28	2.08	1.84	1.73
diphenylether	4.52	1.55	1.34	1.36	1.41	0.80	0.71	1.04	1.14	1.28	0.86	1.63	2.64	3.01	3.95	5.46	4.55	3.37	2.50
3-phenoxytoluene	0.89	0.44	0.33	0.28	0.28	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.08	0.28	0.43	0.57	0.62
4-phenoxytoluene	0.95	0.47	0.40	0.35	0.37	0.05	0.07	0.09	0.09	0.10	0.00	0.08	0.09	0.09	0.15	0.52	0.60	0.68	0.63
Unknown	1.74	1.28	1.35	1.38	1.46	0.87	0.75	0.95	0.96	1.02	0.75	0.89	0.83	0.89	0.93	1.95	2.16	2.68	1.93
Unknown	0.85	0.72	0.85	0.60	0.58	0.25	0.03	0.13	0.13	0.14	0.11	0.07	0.04	0.08	0.08	0.39	0.55	0.71	0.76
Higher Phenols	7.94	6.53	3.70	3.36	2.91	1.16	1.07	1.24	1.22	1.58	0.90	1.80	1.61	1.93	2.54	3.89	4.50	4.70	4.88
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2,3,6 conversion	84.3	77.0	75.0	74.2	73.8	56.8	52.7	54.8	56.7	57.8	50.0	61.7	73.3	74.6	80.1	85.0	83.7	81.9	80.5
Phenol conversion	63.9	52.8	45.2	41.7	40.5	20.7	12.7	16.3	14.6	16.5	12.7	13.8	13.1	13.6	19.8	40.8	44.3	47.3	47.9
Total conversion	74.1	64.8	60.1	57.9	57.1	38.8	32.7	35.4	35.7	37.2	31.3	37.8	43.2	44.1	48.9	62.8	64.0	64.6	64.2
Ave Time	8.825	12.15	11.8	11.305	13.01	12.015	3.725	8.445	3.825	8.44	3.18	8.785	1.485	8.66	11.83	12.86	17.16	11.5	11.985
TOS (hrs)	8.825	29.8	53.75	76.655	101.17	126.195	141.935	154.105	166.175	178.24	189.86	201.825	212.095	222.24	242.73	267.42	297.44	326.1	349.565

Appendix F

Table F7: Results from experiment 7

Component (Mole%)																	
Sample	xt10-1	xt10-2	xt10-3	xt10-4	xt10-5	xt10-6	xt10-7	xt10-8	xt10-9	xt10-10	xt10-11	xt10-12	xt10-13	xt10-14	xt10-15	xt10-16	xt10-17
Time (hrs)	13.1	23.88	43.93	66.1	90.63	114.20	138.23	148.11	154.86	168.11	180.65	191.08	207.21	213.93	229.55	238.8	252.58
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.04
Cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	1.41	0.81	1.19	1.35	1.65	1.48	1.11	0.63	0.54	0.46	0.39	0.31	0.28	0.16	0.17	0.42	0.24
Toluene	0.61	0.47	0.72	0.76	0.81	0.69	0.51	0.26	0.22	0.20	0.16	0.14	0.13	0.08	0.08	0.11	0.07
p-xylene	0.16	0.16	0.25	0.27	0.27	0.22	0.14	0.08	0.07	0.07	0.07	0.06	0.05	0.03	0.02	0.04	0.02
o-xylene	0.00	0.03	0.07	0.07	0.06	0.07	0.06	0.03	0.03	0.02	0.03	0.02	0.02	0.01	0.01	0.02	0.01
Other Lights	0.07	0.07	0.22	0.27	0.23	0.12	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	59.11	49.43	46.34	48.67	51.12	52.74	55.44	63.26	64.06	62.11	62.01	60.91	66.77	67.84	70.78	72.78	73.76
o-cresol	4.91	7.16	7.26	7.01	6.97	6.69	5.41	4.02	3.69	4.36	4.32	4.28	2.86	1.74	1.52	1.29	1.19
2,6 Xylenol	0.85	0.53	0.36	0.39	0.43	0.47	0.76	1.09	1.11	1.04	1.06	1.11	1.18	1.25	1.19	1.11	1.06
p-cresol	1.97	2.74	2.67	2.64	2.53	2.72	2.42	1.99	1.92	2.10	2.00	2.03	1.51	1.05	0.92	0.80	0.76
m-cresol	5.99	8.82	8.75	8.27	8.34	8.19	6.31	4.66	4.35	5.03	5.01	4.90	3.19	2.15	1.75	1.49	1.40
2,4 Xylenol	0.33	0.51	0.40	0.31	0.27	0.27	1.48	2.07	1.99	1.85	1.64	1.80	2.21	2.59	2.46	2.36	2.26
2,5 Xylenol	5.94	2.07	1.26	1.30	1.66	1.63	3.51	4.66	4.61	4.06	4.29	4.34	6.32	8.99	9.12	9.33	9.72
2,4,6-trimethylphenol	0.00	0.21	0.23	0.39	0.11	0.04	0.07	0.05	0.04	0.07	0.06	0.06	0.04	0.00	0.00	0.00	0.00
2,3,-Xylenol	0.92	0.54	0.64	0.46	0.43	0.61	1.73	1.29	1.28	1.23	1.23	1.29	1.29	1.49	1.28	0.48	0.49
3,5-Xylenol	1.54	1.35	0.97	0.94	1.03	1.19	2.14	1.60	1.57	1.67	1.66	1.66	1.39	1.41	1.14	0.63	0.56
2,3,5 trimethylphenol	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4,5 trimethylphenol	0.11	0.10	0.16	0.60	0.52	0.37	0.22	0.18	0.16	0.25	0.17	0.26	0.13	0.48	0.05	0.50	0.45
diphenylether	6.30	8.95	10.38	10.67	9.79	9.47	9.16	8.24	8.46	8.96	9.48	10.06	8.35	7.49	7.16	6.26	5.73
3-phenoxytoluene	0.96	1.75	2.63	2.75	2.21	2.15	1.61	0.86	0.54	0.63	0.56	0.62	0.38	0.18	0.16	0.16	0.14
4-phenoxytoluene	0.90	1.32	1.54	1.56	1.70	1.52	1.19	0.59	0.58	0.63	0.70	0.70	0.45	0.24	0.21	0.19	0.16
Unknown	2.28	3.46	3.69	3.17	2.92	2.71	2.85	1.76	1.67	1.78	1.80	1.63	1.25	0.79	0.69	0.56	0.53
Unknown	0.62	0.99	0.92	0.74	0.81	0.69	0.58	0.22	0.18	0.20	0.19	0.29	0.18	0.06	0.05	0.04	0.03
Higher Phenols	4.89	6.86	9.31	7.36	8.11	5.38	3.50	2.63	2.71	3.25	3.11	3.27	2.01	1.95	1.25	1.41	1.41
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2,6 conversion	64.33	87.57	92.42	92.21	90.03	86.04	78.94	71.94	72.34	75.62	74.28	73.99	82.09	48.07	45.29	44.00	41.71
Phenol conversion	29.07	40.69	44.39	41.60	38.86	36.71	33.48	24.09	23.13	25.47	25.59	26.91	19.87	18.59	15.06	12.67	11.48
Total conversion	34.94	48.50	52.39	50.03	47.22	45.43	41.05	32.06	31.33	33.83	33.70	34.76	28.91	23.17	20.10	17.89	16.52
Ave Time	6.55	5.39	10.025	11.085	12.265	11.785	10.515	4.94	4.875	6.625	6.27	5.215	8.065	3.36	7.81	4.525	6.99
TOS (hrs)	6.55	18.49	33.91	55.02	78.37	102.42	124.72	140.17	149.99	161.49	174.38	185.87	199.15	210.57	221.74	234.08	245.59

Table F (continued)

Component (Mole%)													
Sample	xt10-18	xt10-19	xt10-20	xt10-21	xt10-22	xt10-23	xt10-24	xt10-25	xt10-26	xt10-27	xt10-28	xt10-29	xt10-30
Time (hrs)	277.96	313.83	336.16	359.88	384.30	408.41	432.58	453.18	479.65	502.96	527.03	554.25	578.96
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	0.22	0.41	0.43	0.52	0.67	0.53	0.51	0.43	0.41	0.32	0.62	1.05	0.95
Toluene	0.10	0.14	0.16	0.22	0.27	0.23	0.20	0.16	0.13	0.12	0.26	0.46	0.40
p-xylene	0.04	0.06	0.09	0.10	0.12	0.11	0.09	0.07	0.05	0.06	0.11	0.16	0.16
o-xylene	0.02	0.03	0.04	0.04	0.05	0.05	0.03	0.03	0.02	0.02	0.05	0.06	0.08
Other Lights	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	69.74	62.11	57.77	56.07	55.84	54.31	61.02	63.49	65.97	64.23	56.53	52.08	53.53
o-cresol	1.81	3.74	4.72	5.35	5.66	5.69	4.15	3.12	2.67	2.65	5.09	6.34	6.11
2,6 Xylenol	1.10	1.02	0.86	0.78	0.74	0.66	0.80	0.66	0.94	0.97	0.86	0.44	0.42
p-cresol	1.04	1.63	2.18	2.35	2.44	2.48	1.95	1.48	1.43	1.45	2.23	2.46	2.44
m-cresol	2.03	4.06	5.31	5.96	6.28	6.47	4.58	3.63	3.03	3.10	5.77	7.26	7.25
2,4 Xylenol	2.22	1.85	1.52	1.30	1.19	1.15	1.80	1.34	1.86	2.01	1.20	0.80	0.63
2,5 Xylenol	8.42	4.84	3.57	2.99	2.81	2.67	5.18	7.14	7.37	7.06	3.93	2.30	2.49
2,4,6-trimethylphenol	0.00	0.04	0.07	0.08	0.06	0.08	0.05	0.00	0.00	0.00	0.06	0.06	0.07
2,3,-Xylenol	1.19	1.15	1.05	0.94	0.90	0.82	0.93	1.06	1.12	1.25	0.82	0.58	0.63
3,5-Xylenol	1.16	1.40	1.45	1.39	1.41	1.47	1.22	1.33	1.14	1.33	1.37	1.35	1.41
2,3,5 trimethylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4,5 trimethylphenol	0.15	0.10	0.10	0.10	0.11	0.10	0.10	0.23	0.15	0.25	0.10	0.10	0.12
diphenylether	7.63	11.26	12.30	12.67	12.82	13.09	10.57	9.94	9.39	10.19	13.07	12.80	12.00
3-phenoxytoluene	0.24	0.74	1.10	1.37	1.45	1.52	0.97	0.57	0.52	0.51	1.54	2.19	2.00
4-phenoxytoluene	0.31	0.78	1.04	1.29	1.25	1.27	0.91	0.75	0.57	0.56	1.28	1.63	1.53
Unknown	0.85	1.86	2.08	2.22	2.37	2.42	1.77	1.38	1.24	1.24	2.15	2.50	2.35
Unknown	0.08	0.20	0.29	0.33	0.37	0.39	0.25	0.15	0.12	0.12	0.36	0.50	0.44
Higher Phenols	1.44	2.56	3.63	3.75	3.37	4.49	3.12	2.66	1.85	2.51	3.80	4.86	4.73
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2,6 conversion	49.50	70.93	78.58	82.04	83.14	84.01	68.94	57.19	55.76	57.50	76.40	86.22	85.07
Phenol conversion	18.32	25.47	30.67	32.72	33.23	34.83	28.78	23.81	20.83	22.93	33.36	37.53	35.76
Total conversion	21.85	33.05	38.66	40.94	41.55	43.02	33.80	29.37	26.65	28.69	40.84	45.65	43.96
Ave Time	12.69	17.935	11.165	11.86	12.21	12.055	12.085	10.3	13.235	11.605	12.085	13.61	12.355
TOS (hrs)	265.27	295.90	325.00	348.02	372.09	398.36	420.50	442.86	466.42	491.26	514.95	540.84	566.61

Appendix F

Table F8: Results from experiment 8

Component (Mole%)																	
Sample	xt11-1	xt11-2	xt11-3	xt11-4	xt11-5	xt11-6	xt11-7	xt11-8	xt11-9	xt11-10	xt11-11	xt11-12	xt11-13	xt11-14	xt11-15	xt11-16	xt11-17
Time (hrs)	13.1	23.88	43.93	66.1	90.63	114.20	138.23	145.11	154.68	168.11	180.68	191.08	207.21	213.93	229.55	238.6	252.58
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.04
Cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	0.43	1.50	1.82	1.55	1.35	1.15	0.67	0.62	0.48	0.42	0.34	0.33	0.19	0.15	0.15	0.16	0.26
Toluene	0.16	0.56	5.75	0.42	0.33	0.28	0.21	0.22	0.09	0.11	0.07	0.10	0.06	0.03	0.04	0.06	0.09
p-xylene	0.04	0.23	0.21	0.13	0.10	0.08	0.06	0.05	0.02	0.03	0.00	0.02	0.02	0.00	0.00	0.01	0.02
o-xylene	0.02	0.05	0.04	0.03	0.03	0.03	0.02	0.03	0.00	0.02	0.00	0.02	0.01	0.00	0.00	0.00	0.02
Other Lights	0.00	0.19	0.12	0.06	0.05	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol	80.40	49.68	48.45	54.33	59.80	62.48	71.50	78.06	80.87	80.26	79.74	83.20	86.08	87.18	88.16	87.72	87.80
o-cresol	1.29	2.37	2.23	2.12	2.07	2.06	1.70	1.22	1.12	1.20	1.14	0.75	0.55	0.42	0.40	0.38	0.38
2,6 Xylenol	0.14	0.03	0.00	0.00	0.00	0.06	0.12	0.20	0.20	0.19	0.20	0.20	0.20	0.19	0.18	0.18	0.17
p-cresol	0.50	0.89	0.82	0.76	0.82	0.78	0.71	0.57	0.54	0.55	0.52	0.39	0.28	0.24	0.23	0.23	0.23
m-cresol	1.74	3.22	3.01	2.62	2.74	2.72	2.08	1.55	1.36	1.46	1.42	1.02	0.75	0.85	0.62	0.66	0.65
2,4 Xylenol	0.29	1.76	1.28	0.81	0.57	0.48	0.11	0.30	0.32	0.29	0.28	0.28	0.29	0.25	0.23	0.21	0.17
2,5 Xylenol	2.33	0.43	0.17	0.27	0.35	0.41	0.78	1.39	1.34	1.22	1.32	2.05	2.84	3.10	3.19	3.41	2.96
2,4,6-trimethylphenol	0.11	0.27	0.22	0.18	0.15	0.13	0.09	0.16	0.17	0.17	0.17	0.18	0.18	0.16	0.18	0.18	0.16
2,3-Xylenol	0.80	1.36	1.13	1.01	0.86	0.93	0.72	0.85	0.83	0.82	0.80	0.46	0.37	0.34	0.29	0.31	0.30
2,3,6-trimethylphenol	0.00	0.12	0.11	0.10	0.09	0.08	0.04	0.04	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02
3,5-Xylenol	0.06	0.09	0.07	0.06	0.10	0.11	0.11	0.14	0.15	0.15	0.15	0.11	0.09	0.08	0.06	0.01	0.06
2,3,5-trimethylphenol	0.21	0.52	0.38	0.23	0.15	0.12	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4,5-trimethylphenol	0.00	0.18	0.15	0.15	0.14	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
diphenylether	7.85	19.86	22.60	23.43	21.51	20.18	15.48	10.91	9.73	10.50	11.24	9.07	6.79	6.01	5.21	5.38	5.93
3-phenoxytoluene	0.31	1.66	1.78	1.47	1.13	0.86	0.54	0.22	0.14	0.15	0.16	0.09	0.05	0.04	0.03	0.04	0.04
4-phenoxytoluene	0.30	1.20	1.15	1.00	0.84	0.76	0.51	0.27	0.18	0.19	0.21	0.13	0.08	0.05	0.04	0.04	0.04
9H-Xanthene	0.00	4.52	4.06	3.57	2.92	2.60	1.68	1.37	1.06	1.06	1.05	0.71	0.44	0.37	0.34	0.31	0.36
Xanthone	0.00	0.66	0.52	0.37	0.27	0.21	0.14	0.10	0.06	0.05	0.05	0.03	0.01	0.01	0.01	0.01	0.01
Higher Phenols	3.04	8.44	3.92	5.06	3.73	3.23	2.28	1.70	1.50	1.32	1.30	0.83	0.73	0.68	0.80	0.70	0.52
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2,5 conversion	51.16	90.93	98.40	94.39	92.68	91.33	83.60	76.87	71.82	74.35	72.33	56.86	40.28	34.85	33.02	28.33	37.77
Phenol conversion	15.58	47.84	49.12	42.96	37.42	34.40	24.93	18.02	15.09	15.71	16.27	12.84	9.62	8.48	7.41	7.89	8.02
Total conversion	17.28	49.89	51.37	45.41	40.05	37.11	27.72	20.54	17.79	18.50	18.94	14.75	11.08	9.72	8.63	8.86	9.44
Ave Time	6.55	5.39	10.025	11.065	12.265	11.785	10.515	4.94	4.675	6.625	6.27	5.215	8.065	3.36	7.81	4.525	6.99
TOS (hrs)	6.55	18.49	33.91	55.02	78.37	102.42	124.72	140.17	149.99	161.48	174.38	185.87	199.15	210.57	221.74	234.08	245.59

Table F8 (continued)

Component (Mole%)					
Sample	xt11-18	xt11-19	xt11-20	xt11-21	xt11-22
Time (hrs)	277.96	313.83	336.16	359.88	384.30
Pump Rate	0.01	0.01	0.01	0.01	0.01
Cyclohexane	0.00	0.00	0.00	0.00	0.00
Benzene	0.26	0.36	0.43	0.36	0.38
Toluene	0.09	0.11	0.13	0.11	0.11
p-xylene	0.02	0.03	0.04	0.03	0.03
o-xylene	0.02	0.02	0.03	0.02	0.02
Other Lights	0.00	0.00	0.00	0.00	0.00
Phenol	81.76	77.84	74.73	79.75	77.34
o-cresol	0.82	1.20	1.41	1.10	1.34
2,6 Xylenol	0.19	0.17	1.50	0.15	0.14
p-cresol	0.41	0.52	0.58	0.50	0.57
m-cresol	1.11	1.54	1.84	1.41	1.70
2,4 Xylenol	0.23	0.21	0.20	0.18	0.19
2,5 Xylenol	1.94	1.28	0.96	1.70	1.23
2,4,6-trimethylphenol	0.17	0.17	0.14	0.15	0.13
2,3-Xylenol	0.46	0.55	0.58	0.49	0.54
2,3,6-trimethylphenol	0.00	0.02	0.02	0.02	0.00
3,5-Xylenol	0.12	0.14	0.14	0.11	0.14
2,3,5-trimethylphenol	0.00	0.00	0.00	0.00	0.00
3,4,5-trimethylphenol	0.00	0.00	0.00	0.00	0.00
diphenylether	10.55	13.11	14.67	11.33	13.05
3-phenoxytoluene	0.13	0.23	0.31	0.22	0.30
4-phenoxytoluene	0.14	0.24	0.31	0.23	0.28
9H-Xanthene	0.75	1.06	1.23	0.93	1.12
Xanthone	0.03	0.05	0.07	0.05	0.06
Higher Phenols	0.80	1.36	0.66	1.15	1.34
Total	100.00	100.00	100.00	100.00	100.00
2,5 conversion	59.28	73.60	79.45	84.23	74.27
Phenol conversion	14.15	18.48	21.53	18.26	18.80
Total conversion	16.30	21.11	24.29	18.55	21.44
Ave Time	12.69	17.935	11.165	11.86	12.21
TOS (hrs)	265.27	295.90	325.00	348.02	372.09

Appendix F

Table F9: Results from experiment 9

Component (Mole%)																	
Sample	TFP-1	TFP-2	TFP-3	TFP-4	TFP-5	TFP-6	TFP-7	TFP-8	TFP-9	TFP-10	TFP-11	TFP-12	TFP-13	TFP-14	TFP-15	TFP-16	TFP-17
Time (hrs)	18.53	44.05	63.80	84.7	107.91	117.25	131.48	139.96	155.3	162.53	179.33	191.00	204.91	212.75	229.33	236.75	251.18
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.04	0.04	0.04
Lights	1.15	2.14	2.10	1.63	1.47	1.02	0.71	0.51	0.47	0.36	0.39	0.33	0.22	0.20	0.25	0.20	0.22
Phenol	70.32	52.00	49.27	51.99	58.36	60.32	71.30	73.24	73.66	72.22	75.31	81.04	83.39	84.10	84.52	85.70	84.16
o-cresol	3.03	4.03	3.91	3.89	3.79	3.29	2.29	2.09	1.92	2.26	1.95	1.36	1.21	1.37	1.35	0.99	1.21
2,6 Xylenol	0.52	0.97	0.62	0.49	0.31	0.21	0.08	0.32	0.33	0.45	0.33	0.28	0.26	0.37	0.35	0.25	0.35
p-cresol	1.47	1.93	1.79	1.80	1.81	1.75	1.41	1.25	1.21	1.31	1.25	0.89	0.74	0.76	0.72	0.63	0.67
m-cresol	3.42	4.84	4.46	4.26	4.12	3.76	2.47	2.05	1.86	1.79	1.70	1.12	0.87	0.77	0.75	0.75	0.74
2,4 Xylenol	0.37	0.90	0.77	0.89	0.67	0.33	0.59	0.57	0.54	0.54	0.53	0.42	0.38	0.35	0.34	0.34	0.34
2,5 Xylenol	0.56	0.48	0.36	0.32	0.30	0.33	0.42	0.44	0.45	0.44	0.45	0.55	0.84	0.59	0.63	0.61	0.65
2,4,6-trimethylphenol	0.30	0.43	0.36	0.23	0.18	0.11	0.05	0.31	0.33	0.33	0.35	0.61	0.73	0.73	0.79	0.79	0.83
2,3,6 trimethylphenol	0.82	1.01	0.90	0.74	0.84	0.55	0.32	0.24	0.20	0.19	0.17	0.10	0.03	0.03	0.04	0.03	0.03
2,3 Xylenol	0.70	0.75	0.66	0.70	0.76	0.82	0.76	0.77	0.75	0.75	0.73	0.50	0.43	0.37	0.37	0.35	0.37
3,4 xylenol	0.15	0.11	0.08	0.20	0.10	0.03	0.09	0.09	0.09	0.09	0.03	0.09	0.10	0.09	0.11	0.03	0.11
3,5 Xylenol	0.31	0.15	0.11	0.11	0.12	0.18	0.36	0.42	0.43	0.43	0.42	0.47	0.52	0.48	0.51	0.48	0.54
2,3,5-trimethylphenol	0.23	0.20	0.19	0.17	0.16	0.15	0.32	0.36	0.39	0.40	0.40	0.43	0.48	0.44	0.45	0.44	0.46
2,3,5,6	0.26	0.03	0.11	0.08	0.07	0.05	0.11	0.14	0.14	0.14	0.14	0.26	0.31	0.31	0.31	0.30	0.33
diphenylether	7.97	14.03	18.24	18.42	18.00	17.17	11.90	11.99	11.66	12.29	11.49	6.31	6.76	6.10	5.82	5.69	5.94
3-phenoxytoluene	0.83	1.69	2.04	1.73	1.38	1.13	0.50	0.35	0.29	0.32	0.27	0.15	0.03	0.07	0.03	0.03	0.03
4-phenoxytoluene	0.78	1.03	1.24	1.13	0.95	0.85	0.48	0.42	0.38	0.46	0.37	0.29	0.26	0.24	0.22	0.23	0.29
Unknown	0.18	0.56	0.57	0.43	0.33	0.27	0.13	0.10	0.03	0.09	0.03	0.05	0.04	0.04	0.04	0.03	0.02
Unknown	2.37	4.85	5.22	4.68	4.21	3.94	2.49	2.33	2.05	2.03	1.91	1.32	1.03	0.93	0.90	0.87	0.92
Higher Phenols	4.42	7.90	8.77	6.08	4.28	3.66	3.23	2.00	2.60	3.03	1.66	1.42	1.43	1.62	1.50	1.14	1.74
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Tetramethyls	70.70	93.54	88.55	90.97	92.09	94.44	87.84	85.58	85.62	84.86	85.42	72.48	67.37	67.40	67.43	68.04	65.07
Phenol conversion	29.02	47.50	50.26	47.52	43.09	39.11	28.02	26.06	25.84	27.09	23.96	18.20	15.82	15.10	14.68	13.49	15.04
Total conversion	29.41	47.94	50.62	47.93	43.55	39.63	28.58	26.62	26.20	27.64	24.55	18.71	16.30	15.59	15.18	14.00	15.51
Ave Time	9.265	12.78	9.775	10.55	11.605	4.67	7.115	4.24	7.67	3.815	8.4	5.835	8.955	3.92	8.29	3.71	7.215
TOS (hrs)	9.265	31.29	53.83	74.15	96.31	112.58	124.37	135.72	147.63	158.92	170.93	185.17	197.96	206.83	221.04	233.04	243.97

Table F9 (continued)

Component (Mole%)					
Sample	TFP-18	TFP-19	TFP-20	TFP-21	TFP-22
Time (hrs)	274.83	286.26	323.31	347	372.86
Pump Rate	0.01	0.01	0.01	0.01	0.01
Lights	0.20	0.50	0.72	0.70	0.71
Phenol	62.03	69.86	66.21	66.79	66.52
o-cresol	1.23	2.33	2.77	2.79	3.15
2,6 Xylenol	0.29	0.34	0.32	0.33	0.48
p-cresol	0.80	1.46	1.67	1.66	1.73
m-cresol	1.03	2.36	2.80	2.81	2.72
2,4 Xylenol	0.42	0.54	0.56	0.57	0.57
2,5 Xylenol	0.62	0.32	0.26	0.25	0.25
2,4,6-trimethylphenol	0.71	0.22	0.13	0.12	0.12
2,3,6 trimethylphenol	0.09	0.23	0.28	0.28	0.27
2,3 Xylenol	0.51	0.84	0.90	0.90	0.86
3,4 xylenol	0.10	0.09	0.09	0.09	0.09
3,5 Xylenol	0.52	0.26	0.26	0.19	0.19
2,3,5-trimethylphenol	0.46	0.23	0.18	0.18	0.18
2,3,5,6	0.27	0.03	0.04	0.04	0.04
diphenylether	8.22	14.36	15.48	15.27	14.53
3-phenoxytoluene	0.12	0.49	0.64	0.60	0.58
4-phenoxytoluene	0.04	0.09	0.66	0.66	0.84
Unknown	0.08	0.11	0.14	0.14	0.13
Unknown	1.29	2.44	2.78	2.62	2.69
Higher Phenols	0.97	3.08	3.11	2.62	3.57
Total	100.00	100.00	100.00	100.00	100.00
Tetramethyls	71.16	93.65	96.23	96.12	96.20
Phenol conversion	17.19	29.68	33.16	32.58	32.85
Total conversion	17.70	30.26	33.76	33.18	33.45
Ave Time	11.725	11.815	12.525	11.845	12.525
TOS (hrs)	262.91	286.45	310.79	335.18	359.53

Appendix F

Table F10: Results from experiment 10

Component (Mole%)										
Sample	Tos-1	Tos-2	Tos-3	Tos-4	Tos-5	Tos-6	Tos-7	Tos-8	Tos-9	Tos-10
Time (hrs)	26.98	51.36	76.15	94.8	120.48	141.90	166.16	190.08	216.28	236.43
Pump Rate	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Benzene	0.93	1.29	1.24	0.68	0.70	0.81	0.85	0.71	0.59	0.66
Toluene	0.64	1.00	0.68	0.82	0.86	0.91	0.31	0.75	0.64	0.87
p-xylene	0.25	0.45	0.40	0.41	0.41	0.41	0.77	0.34	0.31	0.32
o-xylene	0.04	0.19	0.18	0.15	0.15	0.18	0.38	0.13	0.11	0.12
Other Lights	0.08	0.09	0.05	0.11	0.29	0.32	0.32	0.25	0.20	0.04
Phenol	30.98	20.92	22.62	24.17	26.70	28.05	28.34	27.75	27.28	27.85
o-cresol	7.91	12.33	11.84	11.10	10.90	10.59	10.28	9.93	9.99	10.27
2,6 Xylenol	1.13	0.13	1.28	1.35	1.51	1.36	1.33	1.11	1.38	1.41
p-cresol	3.89	0.45	4.43	4.68	4.68	4.70	4.60	4.89	4.77	4.87
m-cresol	9.79	15.75	15.28	14.13	14.40	14.50	14.27	13.18	12.72	12.83
2,4 Xylenol	2.37	2.14	2.02	2.55	2.54	2.55	2.38	2.78	3.06	3.12
2,5 Xylenol	20.73	9.06	10.18	10.71	13.03	14.22	15.35	14.10	13.59	13.51
2,3 Xylenol	5.07	6.20	5.74	5.22	4.94	4.56	4.43	4.64	5.27	5.57
2,4,6-trimethylphenol	0.28	0.50	0.46	0.49	0.47	0.43	0.42	0.42	0.48	0.45
3,5 Xylenol	2.09	3.24	3.00	2.74	2.68	2.46	2.18	2.46	2.71	2.74
2,3,5-trimethylphenol	0.27	0.50	0.47	0.51	0.51	0.47	0.43	0.47	0.52	0.50
3,4,5-trimethylphenol	0.92	1.55	1.50	0.89	0.97	0.66	1.28	0.87	0.91	1.24
diphenylether	2.22	2.57	2.42	2.09	1.89	1.77	1.82	1.94	2.25	2.42
3-phenoxytoluene	0.99	1.80	1.71	1.89	1.54	1.39	1.41	1.48	1.59	1.64
4-phenoxytoluene	0.80	1.17	1.21	1.13	1.04	0.99	0.99	1.03	1.11	1.15
Unknown	1.55	2.08	1.83	1.55	1.34	1.25	1.30	1.35	1.47	1.46
Unknown	1.58	2.60	2.35	2.05	1.64	1.46	1.54	1.63	1.72	1.60
Higher Phenols	5.49	14.21	8.95	10.76	8.82	5.72	5.01	7.80	7.34	5.56
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2,5 conversion	58.54	81.89	79.68	78.57	73.95	71.56	69.31	71.80	72.82	72.98
Phenol conversion	38.04	58.16	54.77	51.66	48.80	43.90	43.32	44.49	45.43	44.29
Total conversion	48.29	70.02	67.22	65.12	60.27	57.73	56.31	58.15	59.13	58.64
Ave Time	13.49	12.19	9.395	12.325	12.64	10.71	12.13	11.92	13.14	10.075
TOS (hrs)	13.49	39.17	60.76	82.48	107.64	131.19	154.03	178.08	203.14	226.36

Table F11: Results from experiment 11

Component (Mole %)								
	2,5-iso	2,5-iso	2,5-iso	2,5-iso	2,5-iso	2,5-iso	2,5-iso	2,5-iso
Sample	kop-xyl-4	kop-xyl-5	kop-xyl-15	kop-xyl-16	kop-xyl-8	kop-xyl-9	kop-xyl-12	kop-xyl-13
Pump Rate	0.02	0.02	0.02	0.02	0.08	0.08	0.08	0.08
2,6-xylenol	20.98	10.22	11.00	11.81	10.03	10.12	10.15	10.24
2,4-xylenol	9.11	20.49	21.23	21.54	21.92	21.89	21.89	21.76
2,5-xylenol	18.50	31.91	28.33	28.03	32.47	31.53	31.13	30.54
2,3-xylenol	30.12	10.31	10.03	10.01	10.17	10.27	10.44	10.47
3,5-xylenol	9.14	13.82	15.77	15.46	13.32	13.81	13.73	14.04
3,4-xylenol	12.17	13.24	13.58	13.35	12.06	12.77	12.86	12.94
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00