Isomerisation of Cresols

over

zeolites HZSM5, HBeta and HMordenite

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SYNOPSIS

In the natural (phenolic material obtained from coal) phenolics industry two problems are experienced with regards to cresol isomers. Firstly, insufficient quantities are recovered from natural sources such as coal tar and refinery caustics and secondly the isomer distribution is inflexible and does not always meet market demand. Thus, having technology which provides alternative routes to certain cresol isomers is of utmost importance to natural cresol producers. The isomerisation of one cresol isomer into one or more of the others would enable a producer to swing (to a limited extent) the distribution of isomers to suite the demand of customers. For this study, the isomerisation and disproportionation of the three cresol isomers were investigated over three types of zeolites under liquid as well as vapour phase (only o-cresol isomer) reaction conditions.

The best activity for o-cresol isomerisation, in the liquid phase, was initially HMordenite but because the catalyst deactivates so quickly, HZSM5 was thus regarded as the best catalyst. HZSM5 gave the best activity for both m- and p-cresol isomerisation in the liquid phase. The activity over HBeta was between that of HZSM5 and HMordenite for all the cresol isomer conversions. Expected from the shape selectivity of the zeolite, the best isomerisation selectivity (>86.0%) was obtained with HZSM5. HBeta gave both isomerisation and disproportionation but the favored pathway is disproportionation, while HMordenite, due to the deactivation, proved to be suitable for neither isomerisation nor disproportionation. It can thus be concluded that HZSM5 gave the best conversion for o-, m- and p-cresol in terms of the desired isomerised products and that it is the preferred catalyst for isomerisation in the liquid phase.

The average activity for o-cresol conversion in the vapour phase followed the order HZSM5 > HBeta ≈ HMordenite. HZSM5 proved to be the best isomerisation catalyst for o-cresol and high selectivity (>95%) and stability was obtained over five days on stream, while HBeta showed a gradual decline in isomerisation selectivity and stability. A rapid decrease was noticeable over HMordenite in terms of selectivity and stability. The activity, stability and

isomerisation selectivity data obtained, is therefore conclusive with regards to HZSM5 being the preferred zeolite for isomerisation of o-cresol.

Further work could entail optimisation of the p-selectivity, from o-cresol and m-cresol transformation, and lifetime studies of the preferred zeolite HZSM5. It is thus recommended to investigate CVD (chemical vapour deposition) to deactivate the external surface of the catalyst as well as noble metal impregnation and/or the use of hydrogen as a carrier gas.

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TABLE OF CONTENTS

LIST OF SCHEMES

LIST OF FIGURES

Page

LIST OF TABLES

GLOSSARY

LHSV	Liquid Hour Space Velocity
FCC	Fluid Catalytic Cracking
ECN resin	Epoxy-o-cresol novolak resin
COC	p-chloro-o-cresol or 4-chloro-o-cresol
BHT	2,6-di-tert-butyl-p-cresol/2,6-di-tert-butyl-hydroxy-toluene
TCP	Tricresyl phosphates
Si/Al ratio	Silica-alumina ratio
CVD	Chemical vapour deposition
HPLC	High pressure liquid chromatography
GC	Gas chromatography
HP	Hewlett Packard
RF	Response Factors
rpm	revolutions per minute
psig	Pounds per square inch
I/D	Isomerisation to Disproportionation
TOS	Time-on-stream

1. INTRODUCTION

In the phenolics industry two problems are experienced with regards to cresol isomers. Firstly, insufficient quantities are recovered from natural sources such as coal tar and refinery caustics and secondly the isomer distribution is invariable and not ideal.

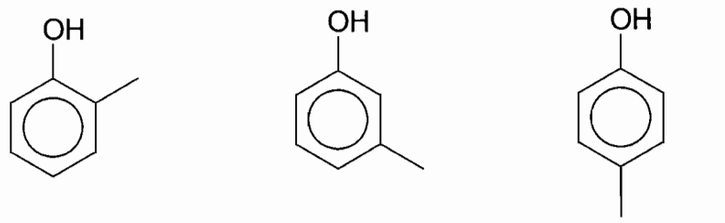
Since phenolic material, which originates from "natural" sources such as coal tar and refinery caustics, has a specific carbon number and isomer distribution, producers in this field have the problem that their original isomer distribution does not always meet the demand of customers for the various isomers. This results in a huge demand for specific isomers, which the producers from natural sources cannot supply.

Thus, having technology, which provides alternative routes to selective cresols, available is of the utmost importance. The isomerisation of o-cresol into m- and p-cresol would enable a producer to swing (to a limited extent) the distribution of isomers to suit the demand of customers. Merisol [Joint venture formed in 1997 between Merichem, based in the United States, and Sasol Phenolics in South Africa] can benefit from such technology to produce the more expensive m- and p-cresols. For this study, the isomerisation of cresols was investigated over various types of zeolites.

2. LITERATURE OVERVIEW

2.1 Introduction

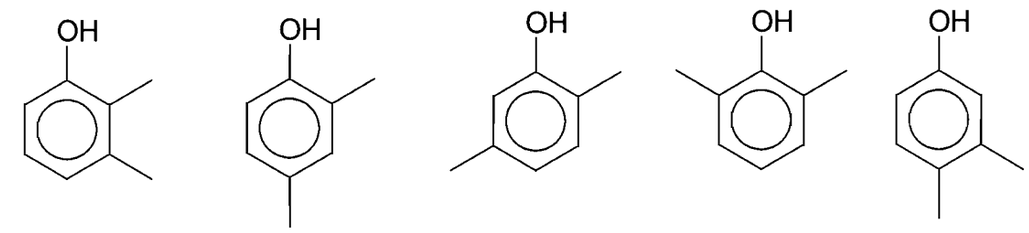
Cresol, methylphenol, occurs in three isomeric forms: ortho-, meta- and para-cresol (Scheme 2.1). Mixtures of m- and p-cresol and of o-, m- and p-cresol are



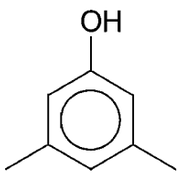
o-Cresol m-Cresol p-Cresol

Scheme 2.1 Isomeric forms of cresol

occasionally referred to in technical literature as dicresol and tri- or isocresol respectively, while xylenol, dimethylphenol, occurs in six isomeric forms i.e. 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethyl phenols[1] (Scheme 2.2).



2.3-Xylenol 2.4-Xylenol 2.5-Xylenol 2.6-Xylenol 3.4-Xylenol



3.5-Xylenol

Scheme 2.2 Isomeric forms of xylenol

2.2 Applications of cresols

Highly pure o-cresol is increasingly processed to epoxy-o-cresol novolak resins (ECN resins), which are used as sealing materials for integrated circuits. Most of the o-cresol produced in Europe is chlorinated to 4-chloro-o-cresol (PCOC), the starting material for chlorophenoxyalkonoic acids. These acids are important as selective herbicides. o-Cresol is also important as a precursor of various dye intermediates. An appreciable amount of o-cresol is used as solvent, either directly, or after hydrogenation to 2-methylcyclohexanol or 2-methylcyclohexanone. In the form of its carbonate ester, o-cresol constitutes a starting material in the synthesis of coumarin. The alkylation of o-cresol with propene gives carvacrol, which is used as an antiseptic and in fragrances. Small amounts of o-cresol are used as starting material in the production of various antioxidants.

m-Cresol, either pure or mixed with p-cresol, forms a starting material for important contact insecticides such as *O,O*-dimethyl-*O*-(3-methyl-4-nitrophenyl)thionophosphoric acid and *O,O*-dimethyl-*O*-(3-methyl-methylthiophenyl)thionophosphoric acid ester. Pure m-cresol has considerable

importance in the production of fragrances and flavour substances. Japan uses m-cresol primarily for pesticides while the major outlet for m-cresol in Western Europe is antioxidants and the United States use m-cresol for both applications. Selective methylation of pure m-cresol with methanol gives 2,3,6-trimethylphenol , which is an important starting material in the production of vitamin E and it also serves as a comonomer for the modification of poly(phenylene oxide) resins.

p-Cresol, pure or mixed with m-cresol, is used mainly to produce 2,6-di-tert-butyl-p-cresol (BHT), a nonstaining and light resistant antioxidant. All three major industrial regions (Japan, Western Europe and the United States), use a large amount of BHT and other antioxidants. A growing use for p-cresol is as an intermediate in the production of p-cresol methyl ether, which in turn is converted to p-anisaldehyde.

An important field of application for technical cresol mixtures is the production of modified phenolic resins by condensation with formaldehyde. Cresol mixtures are highly important as solvents for synthetic resin coatings (wire enamels).

m/p-Cresol mixtures are used to produce neutral phosphoric acids esters such as tricresyl phosphate (TCP) and diphenyl cresyl phosphate. These are used as fire-resistant hydraulic fluids, additives in lubricants, air filter oils and flame-retardant plasticizers[2]

2.3 Sources of natural cresols and xylenols

2.3.1 Isolation from Coal Tars

Coal tars are produced as a by-product of the coking of coal and low temperature gasification of coal to produce synthesis gas (e.g. Lurgi gasifier) and resulting removal of sulphur nitrogen bases. Today the largest source of natural cresols and xylenols is provided by the liquid by-products obtained by Sasol in the pressure gasification of bituminous coal and this is similar in composition to low temperature tars.

When the starting material is high temperature tar, the phenols are isolated by extraction with sodium hydroxide solution or, in the Lurgi phenoraffin process from the carbolic oil, light oil and the filtrate of the naphthalene oil. The hydrocarbons and pyridine still present in the crude phenolate caustic are removed by steam distillation and the crude phenol is then liberated with carbon dioxide. The phenolate caustics, which contain primarily phenol and cresol and very small amounts of xylenols, from coking plant effluent are frequently incorporated.

After scrubbing with water, the crude phenol is dehydrated azeotropically and rectified under vacuum into the following fractions: phenol, o-cresol, m/p-cresol, xylenols and phenol tar[1]. For further purification of cresylic acid fractions from neutral oils, tar bases, sulphur compounds, and undesirable phenolic compounds, an extractive distillation with diethylene glycol and water was developed.

2.3.2 Recovery from Spent Refinery Caustics

Cresols and xylenols are obtained partly from the naphtha fractions produced by catalytic and thermal cracking in the petroleum industry in the United States. The composition of the spent cresylate caustics fluctuates widely and they contain on average phenols and 10-15% sulphur compounds. The caustics were collected by reprocessing firms such as Merichem and Northwest Petrochemical and reprocessed in central plants by a variety of processes and due to competition, especially from synthetic o-cresol producers and increased environmental restrictions, the only processor of spent refinery caustics in the United States was Merichem. Due to the synthetic producers, nitrogen containing base and sulphur removal was imperative and the thiols, in the alkaline solution, was first oxidised with air to give disulphides which were decanted as an oily layer.

Merichem precipitates the phenols from caustics with hydrogen sulphide, a waste product of the refineries in Houston. After extraction with a solvent, the sulphide solution obtained in this process is concentrated in a triple effect evaporator to

give sodium sulphide for use in the paper industry and in ore dressing. The water vapour condensate is stripped with natural gas to remove the odorous compounds after which it is passed to a cooling tower. The crude phenol thus precipitated, is removed by distillation and extracted continuously in a countercurrent extraction and the cresylic acids recovered by fractional distillation[1] . In 1996 the cresylic acid capacity of Merichem was approximately 55 000 t/a and this includes phenol, the xylenols and several other alkylphenols.

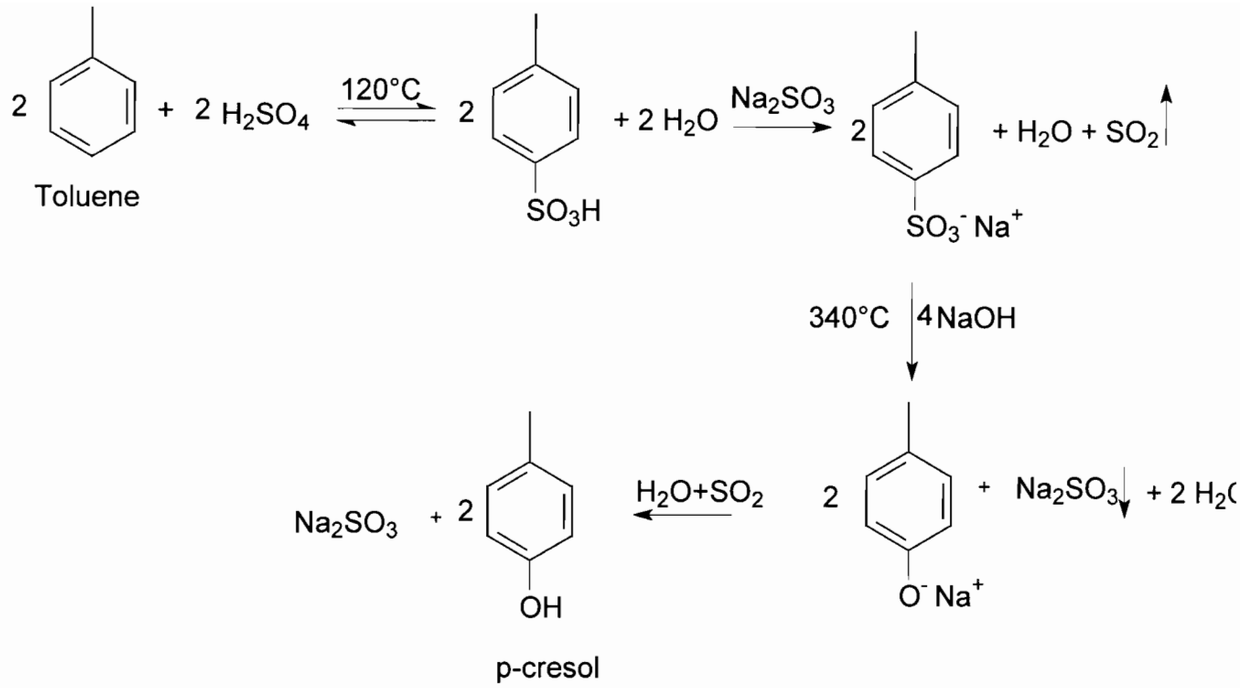
2.4 Synthetic cresols

2.4.1 Production of cresol mixtures from alkyl benzenes and phenol

Cresols can be produced via several synthetic processes, many of which resemble those for phenol. These processes were developed due to insufficient cresol recovery, from coal tars and spent refinery caustics, to meet the rising demand for these cresol isomers. Specific isomers or mixtures of a few phenolics are produced rather than crude blends. The following is a brief discussion of these synthetic routes.

i) Alkali fusion of toluenesulfonates

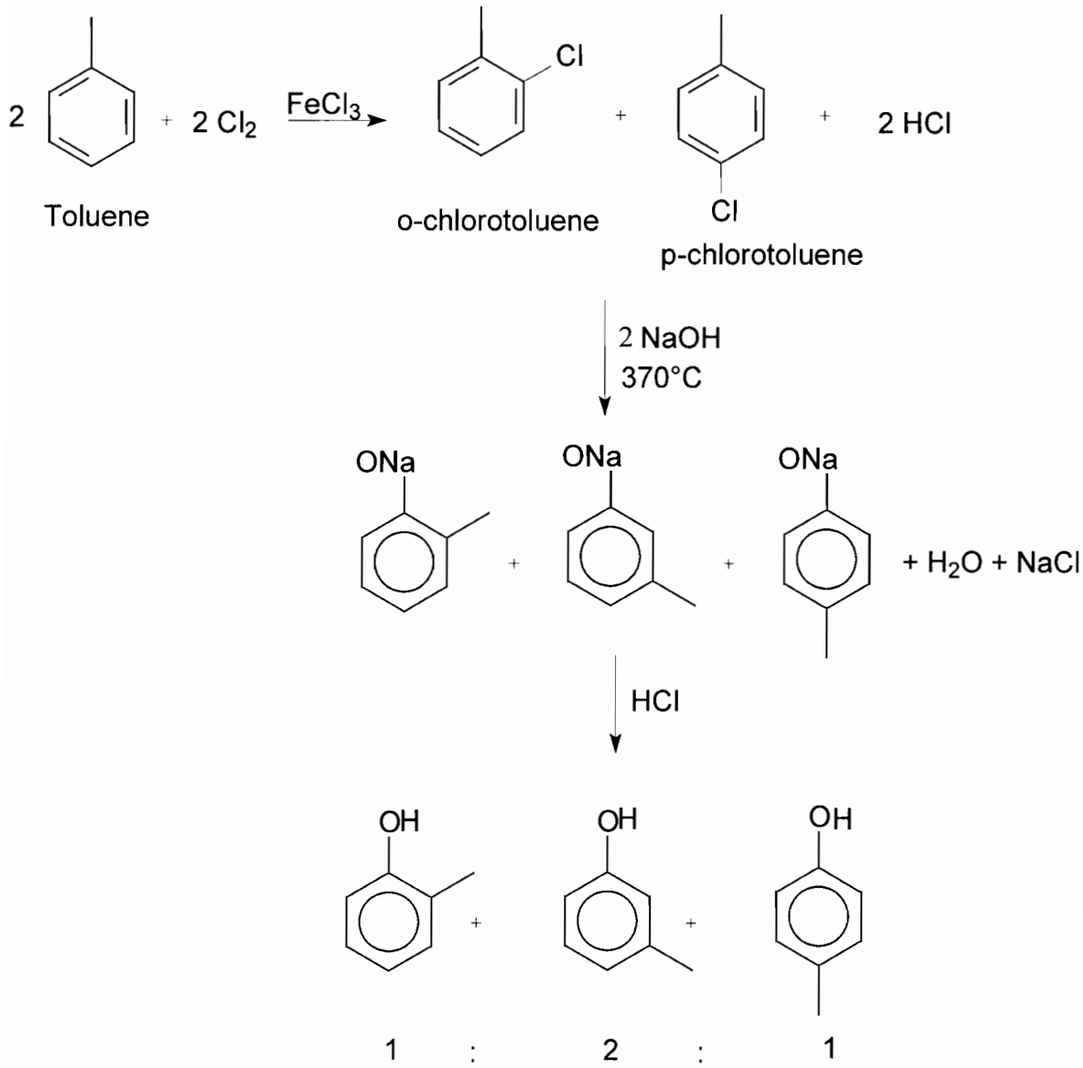
This process is used for the production of cresols with high p-cresol content. Cresols can be produced by the sulfonation of toluene, followed by caustic fusion and subsequent hydrolysis through acidification (Scheme 2.3). The isomer distribution of the cresol mixture is mainly dependent on the sulfonation conditions. A typical raw mix of about 6-12% o-cresol, 6-12% m-cresol and 80-85% p-cresol can be obtained and the cresol yield based on toluene is 80-90%. The disadvantage of this process is the co-production of huge quantities of inorganic salts, which are expensive to dispose off. PMC in the United States, Konan Chemicals in Japan and Synthetic Chemicals in the United Kingdom utilise this process[3, 4].



Scheme 2.3 Alkali fusion of toluenesulfonates

ii) Alkali hydrolysis of chlorotoluene

This is an important process for the production of cresol mixtures with high m-cresol content. This technology resembles the process used to produce phenol from chlorobenzene. Toluene is chlorinated to (o, p)-chlorotoluene, followed by hydrolysis with sodium hydroxide to obtain an isomeric mixture (o, m, p) of the cresols in the approximate ratio 1:2:1 respectively (Scheme 2.4). This ratio differs from that of the chlorotoluene starting material, because isomerisation via aryne intermediates is assumed to occur under the severe conditions of hydrolysis and the yield based on chlorotoluene is ca 80%. The disadvantage is the use of chlorine and co-production of HCl and NaCl. Bayer at Leverkusen, Germany is utilising this process[1, 5, 6, 7].



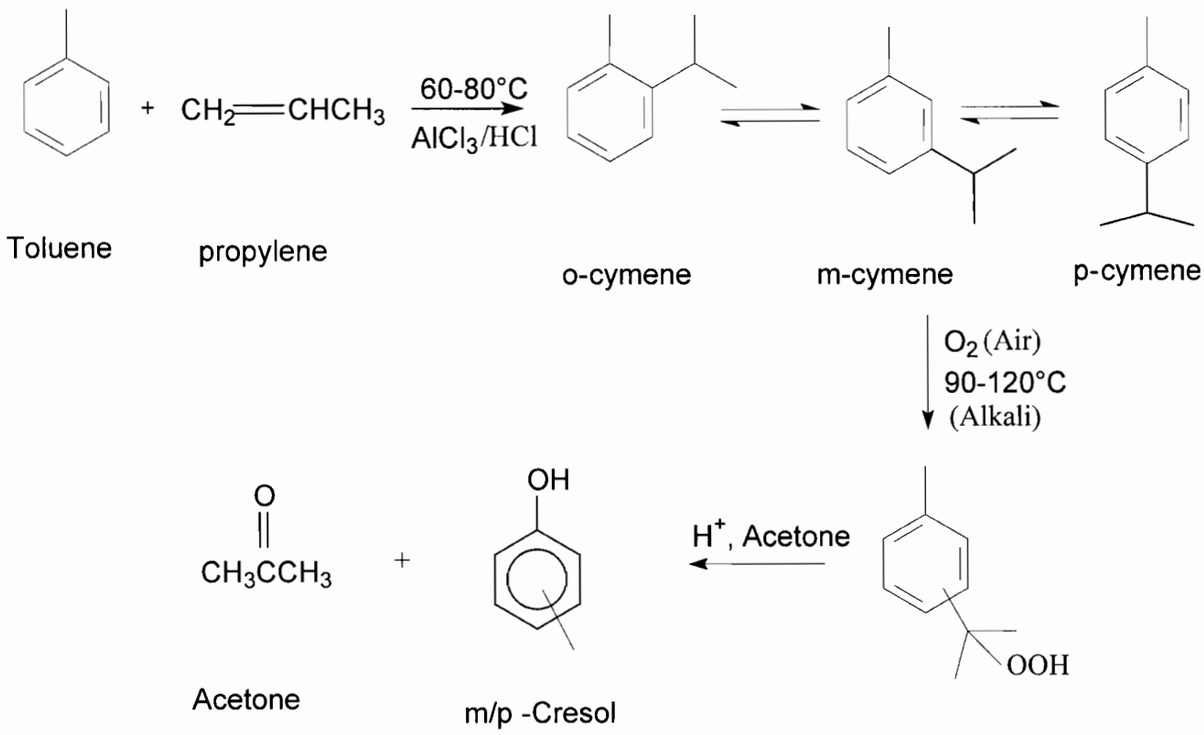
Scheme 2.4 Alkali hydrolysis of Chlorotoluene

iii) Cymene hydroperoxide cleavage

This process permits the production of m- or p-cresol from the corresponding cymenes. This technology resembles the Hock cumene/phenol process and the process consists of three reaction steps: Toluene propylation and cymene isomerisation, oxidation of cymene to cymene hydroperoxide and peroxide cleavage (Scheme 2.5).

All three isomers, o-, m- and p-cymene, are formed in the propylation of toluene but for continuous oxidation , the o-cymene content of the cymene mixture must be kept below 10% at all times. The lowest o-cymene content is that of a cymene mixture in thermodynamic equilibrium and aluminium chloride must be used to reach this equilibrium as quickly as possible. The isomer ratio obtainable with aluminium chloride under practical conditions is ca. 3% o-, 64% m- and 33% p-cymene. In addition, the cymenes can be oxidised up to a peroxide content of only 20% and the methyl group of the cymene is likewise oxidised.

Disadvantages involve considerably more costly distillation procedures and more extensive treatment of wastewater. Mitsui Chemicals and Sumitomo Chemical in Japan use this technology[1].



Scheme 2.5 Cymene hydroperoxide cleavage

iv) Methylation of Phenol

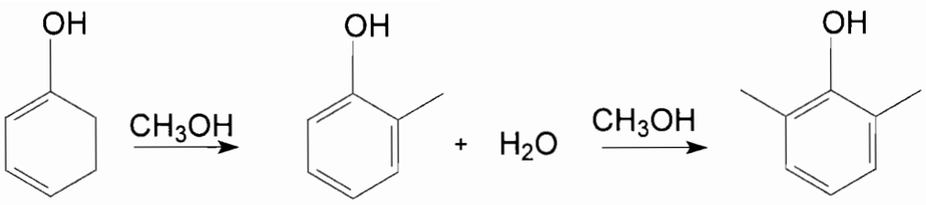
Synthetic cresol, especially o-cresol, and xylenols are now largely produced by methylation of phenol and methanol in the presence of catalysts. The process consists of only one reaction step, but is based on phenol, which is relatively expensive; the separation of products from the reaction mixture is also costly. This is partly because the boiling points of several components are very near to one another and partly because in some cases the purity of the product must meet very strict requirements.

The reaction can be carried out either in the vapour phase or in the liquid phase.

a) Vapour phase methylation

Vapour phase methylation is mainly used to produce pure o-cresol and/or 2,6-xylenol (Scheme 2.6). At atmospheric, or slightly elevated, pressure over a metal oxide catalyst fixed in a multitubular reactor of stainless steel, the methylation is carried out at a temperature of 300-460°C. The reaction temperature required depends on the nature of the catalyst and on the desired composition of the product. Examples of the metal oxides and phenol conversions are: Magnesium oxide (82%), manganese/chromium/vanadium/iron oxide (93-99%), gamma-aluminum oxide (33%), gamma alumina (60%) and aluminium oxides with strong acid sites, silica-alumina, zeolites, aluminium phosphates and phosphoric acid.

General Electric in the United States and Western Europe, GEM Polymers, Nippon Crenol and Mitsubishi Gas Chemical in Japan use this process[8, 9, 10, 11] .



Side reactions:

$CH_3OH \longrightarrow CO + 2\ H_2O$

$CO + H_2O \longrightarrow CO_2 + H_2$

$CO + 3\ H_2 \longrightarrow CH_4 + H_2O$

Scheme 2.6 Methylation of phenol

b) Liquid phase methylation

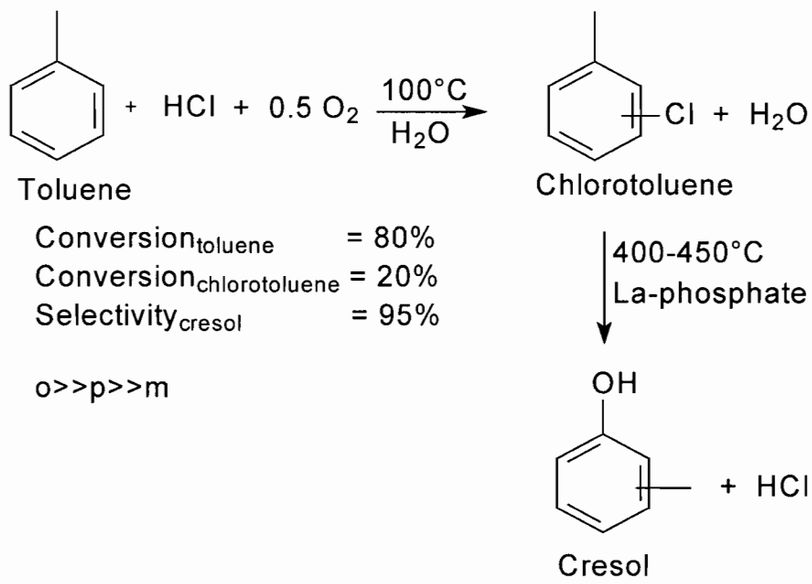
Results similar to those achieved in the vapour phase are obtained if the oxide catalysts (especially gamma-alumina) are suspended in a phenol-methanol mixture and heated in an autoclave at 300-400°C and ca 35 bar.

Chemische Werke Lowi GmbH & Co. has a similar process starting with phenol and equimolar quantities of methanol in a multipurpose autoclave using aluminium methylate as catalyst[1, 2]. The cresol and xylenols yield is about 80% with a phenol conversion of 60%.

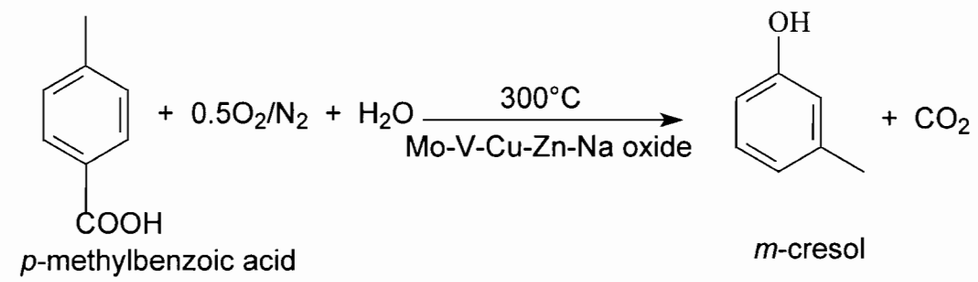
DEA-Mineraloel operated the Biller process where they use an aqueous zinc halide-hydrogen halide solution at 200-240°C and 25 bar and yields of up to 98% were obtained based on converted phenol. The main products were o- and p-cresol, 2,4- and 2,6-xylenol and the ratio was 7 : 5 : 2 : 1 respectively.

vi) Other processes

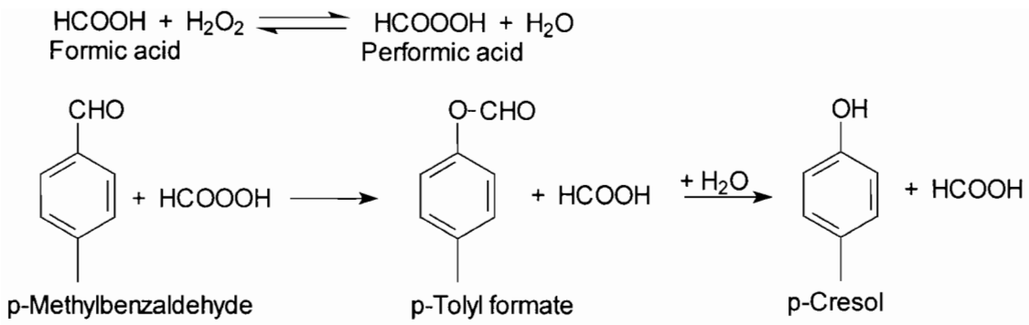
Other routes to the synthesis of cresol appears to not be yet used industrially. These processes include the Gulf oxychlorination process[12, 13] (Scheme 2.7), oxidative decarboxylation of methylbenzoic acids[14, 15] (Scheme 2.8) and the Baeyer-Villiger oxidation[16] of p- or o- methylbenzaldehyde (Scheme 2.9).



Scheme 2.7 Gulf oxychlorination process (over Pd- or Cu-salts and catalytic amounts of nitric acid)



Scheme 2.8 Oxidative decarboxylation of methylbenzoic acids



Scheme 2.9 Baeyer-Villiger oxidation of p- or o-methylbenzaldehyde

v) Summary

The methylation of phenol (iv) is the major process for the production of o-cresol, while the alkali fusion of toluenesulfonates (i) predominates p-cresol manufacture. The major route to m-cresol is the alkali hydrolysis of chlorotoluene (ii) and the major route to m/p-cresol is cymene hydroperoxide cleavage (iii).

2.5 Production of cresols by isomerisation

2.5.1 Introduction

A variety of catalysts have been used over the years to isomerise cresols and the interest in particular catalyst systems can be ascribed to certain periods, e.g. $AlCl_3$ and other Friedel-Craft type of catalysts until the 1950's and zeolites since the 1980's. A summary of the literature, with regards to the different catalyst groups, is described below.

2.5.2 Friedel-Crafts catalysts

Experiments by Norris and Turner[17], as early as 1939, showed that appreciable amounts of m-cresol were formed when p-cresol and $AlCl_3$, in a molar ratio of 1:2, were heated to 200°C. Baddeley[18] observed that an excess of $AlCl_3$ is needed for the isomerisation of phenols. p-Cresol was isomerised at 135°C to an equilibrium mixture of 60.8% m- and 39.2% p-cresol. The same result was obtained when m-cresol was isomerised. No o-cresol was observed during the

isomerisation of p- and m-cresol, while o-cresol isomerisation showed no results. Meissner and French[19] also confirmed that a molar ratio of 1:2 for cresol : $AlCl_3$ is needed for the isomerisation. The same equilibrium mixture (60.5, 21.5 and 18.0% for m-, p- and o-cresol respectively) was obtained when all three isomers are converted at 134°C. Cresol equilibrium ratios of para and meta were almost established within 10 hours when starting with m- or p-cresol. o-Cresol required about 40 hours to reach the same point. The formation of disproportionation products and tar was more rapid with o-cresol than with m- and p-cresol. Meissner and French proved that the finding of Baddeley was incorrect but the isomerisation of o-cresol was indeed slow. Experiments by Fury[20], using the same molar ratio and conditions as Meissner and French, reports a shift in the equilibrium mixture (80 and 20% respectively for m-and p-cresol) by saturating the starting materials in hydrochloric acid. Hydrogen fluoride and boron trifluoride failed to isomerise p-cresol.

A patent to Biller[21] was issued for the isomerisation and transalkylation of alkyl phenols over zinc bromide in the presence of hydrogen bromide and methane sulphonic acid. When o-isopropyl phenol was used, m/p ratio of up to 1.9 was reported with a 92% conversion. Although a high m/p ratio is reported, isomerisation and transalkylation occurred in almost a 1:1 ratio.

Strikingly, the three papers (Baddeley, Meissner and French and Fury) reported three different m/p-cresol ratios, 60.8/39.2, 60.5/21.5 and 80/20 respectively, obtained at a very similar temperature of about 135°C and they found that pressure has no effect on the isomerisation. The reaction takes place only after more than one mole of aluminium chloride has been added to one mole of cresol and involves $AlCl_3$•cresol complexes present in the reaction mixture.

$$CH_3C_6H_2OH + AlCl_3 \Leftrightarrow CH_3C_6H_4OAlCl_2 + HCl$$

After the reaction is finished, the complexes are broken by hydrolysis with water.

$$CH_3C_6H_4OAlCl_2 + 3H_2O \Leftrightarrow CH_3C_6H_2OH + 2HCl + Al(OH)_2$$

Apparently these discrepancies obtained between the m/p-cresol "equilibrium" ratios reported, reflected the stabilities of the $AlCl_3$•cresol complexes involved in the reaction mixtures more than the stabilities of cresol isomers as such. A point to note is that $AlCl_3$ doesn't act as a "catalyst" in this reaction but rather as a reactant that is eventually consumed.

2.5.3 Liquid acids

A patent was issued to Giolito and Mirviss[22] for the preparation of meta-alkylated phenols. The isomerisation of C_2-C_{12} alkylphenols using strong acids such as trifluoromethane sulfonic acid is described. Only 0.5-2.0% by weight trifluoromethane sulfonic acid was needed at 120-190°C. The isomeric composition showed predominance for the meta isomers. Olin[23] used sulphuric and phosphoric acid for the isomerisation of alkylphenols and a meta rich stream is produced. This process works well for tert-alkyl phenol and to some extent for sec-alkyl phenols but no claims are mentioned for the methyl phenols.

2.5.4 Non-zeolitic solid heterogenised acids

Nickels[24] used aluminium fluoride, fluorosilicate or fluoroborate at 500°C and LHSV of 0.23 hr^{-1} to isomerise o-cresol. The resulting distribution, over aluminium fluoride, was found to be 61.4% unreacted o-cresol, 19.6% m- and p-cresol (m/p = 62/32) and 19% disproportionation products, carbon and gas. Nickels also noted that a greater selectivity for the meta position was observed for ethyl phenols. The high activity in promoting isomerisation catalysis of alkylphenols and the low vapour pressure and insolubility in most organic compounds, makes aluminium fluorides attractive catalysts for isomerisation. However, the 50% selectivity towards by-products appears not very attractive.

Neuworth[25, 26] utilised a silica alumina catalyst (88% silica and 12% alumina) with regards to isomerisation experiments. This work was done at temperatures between 288°C and 344°C. Of the three isomeric cresols, the highest reactivity was obtained with p-cresol. The selectivity towards the other cresol isomers was

between 30 and 40%, disproportionation was the major reaction (35 - 55%) besides significant polymerisation and coking (15-30%). The m/p-cresol ratio in the isomerised cresols obtained from o-cresol increased from 2.5 to 13.6 with increasing space velocity.

Kohn and Stevick[27] used Bentonite, activated clay, for the isomerisation of higher alkylphenols at 150-180°C. The preferred end product was the meta isomer. It was observed that under the conditions applicable for isomerising phenols with large alkyl groups, cresols were quite stable and unchanged.

2.5.5 Zeolite catalysts

2.5.5.1 Introduction

A variety of acid catalysts were used over the years to isomerise cresols and the results obtained were unsatisfactory due to the resinification and disproportionation that occurred in addition to isomerisation. Isomerisation without substantial disproportionation is possible on certain acid zeolites of the ZSM group.

Zeolites are highly crystalline alumino-silicate molecular sieves, highly porous with pores of molecular dimensions. They exhibit pore sizes[28] from 0.3~1.0nm and they occur naturally or are synthetic.

Zeolites have the following useful properties:

- Catalytically active
- Molecular sieving
- Have ion-exchange capacity
- High adsorption capacity
- Thermally stable

- Resistant to chemical attack
- Easy to handle
- Non-corrosive

2.5.5.2 Structure of zeolites

Zeolites consist of a framework[29] of AlO_4 and SiO_4 tetrahedra (primary building blocks) linked by the oxygen atoms and each AlO_4 tetrahedron has negative charge, balanced by cations, i.e. Na^+. These cations are mobile and can undergo ion exchange with protons (H^+) and give rise to Brønsted acid sites. Dehydroxylation of Brønsted acid sites forms Lewis acidity. Lewis acidity in zeolites (H-form) is also associated with aluminium species dislodged from the framework. The exact nature of these species and the role of Lewis acid sites in catalysis remain an unsettled issue.

Table 2.1 Typical structure/pore sizes[29, 30] of some technical zeolites

Zeolite		Plane	Pore size (Å)	Framework density	Si/Al* ratio
10 membered rings					
ZSM5		[010]	5.3 x 5.6	17.9 T/1000 Å^3	45
		[100]	5.1 x 5.5		
8 & 12 membered rings					
Mordenite	8	[010]	2.6 x 5.7	17.2 T/1000 Å^3	
	12	[001]	6.5 x 7.0		40
12 membered rings					
Beta		[100]	5.5 x 5.5	15.0 T/1000 Å^3	25
		[001]	7.6 x 6.4		

* The higher the ratio, the smaller the Al content

2.5.5.3 Synthesis of Zeolites

As zeolite structures are built from SiO_4 and AlO_4 tetrahedra these primary building blocks must also be present in the synthesis mixture. Aluminate ions are only stable at high pH values therefore zeolite synthesis is always taking place

from basic solutions. An important factor determining the synthesis conditions is the Si/Al ratio of the zeolite to be synthesised. The higher the Si/Al ratio, the lower the aluminium content and the more difficult the synthesis, resulting into more severe conditions being needed.

The following main steps occur during acid zeolite synthesis[30, 31, 32].

- Preparation of the synthesis hydrogel. This consists of a silica source, an aluminium source, water, hydroxyl groups and inorganic cations (e.g. basic hydroxides such as NaOH) and optionally organic additives (templates)
- Ageing or ripening
- Crystallisation at the desired temperature, induced by nucleation or by seeding. Temperature ranges are generally between 60°C and 200°C.
- Separation from the mother liquor by decanting, filtration or centrifugation, followed by washing and drying.
- Detemplation. This involves removal of the organic template, if present, in the zeolite and it occurs by burning off at about 500°C in oxygen or a mixture of oxygen and an inert gas such as nitrogen.
- Ion exchange. This is where the cations such as sodium or potassium are replaced with ammonia ions. Subsequent calcination converts the ammonium ion to a proton.

Key parameters governing zeolitisation are the molar composition of the gel, alkalinity, temperature and time, templates and seeding.

The possible post-synthesis treatments are as follows:

- Hydrothermal treatment (steaming). Aluminium is leached out of the framework leading to extra framework aluminium within the pores of the zeolite.

- Acid leaching. The removal of framework and or extra framework aluminium from the zeolite using acid.

- Silylation treatment with $SiCl_4$. Substitution of framework aluminium with silicon.

- Silanisation with e.g. alkoxy silanes. Covering of acid sites with inert silica layer preferentially on the external surface of the zeolite crystals.

- For technical catalytic applications the zeolite crystals are formed, typically to extrudates using a binder, e.g. alumina.

2.5.5.4 Reactions over various zeolites

The first patent that was awarded for catalytic isomerisation of o-cresol over zeolite catalyst was in 1979 to URBK. Keim and Kiauk patented a catalytic liquid phase isomerisation process for o-cresol using zeolite ZSM5, ZSM11 and ZSM12[33, 34] at 380-420°C and pressure of 50-60 bar. The best o-cresol conversion obtained was 66.7% with m/p-ratio of 2.7 and 4.8% phenols and 4.1% xylenols reported as byproducts when ZSM11 was used. ZSM5 and ZSM12 gave o-cresol conversion of 53 and 47% respectively with m/p-ratio of 2.4 and 2.5. Less byproducts were formed over ZSM5 (3.0%) and ZSM12 (7.6%) and the catalysts are slowly deactivated by carbon deposition in the course of the reaction.

Engel, Malloy and Shoffner[35, 36] (1985) also used zeolite ZSM5 and the essence of this invention is that by operating under hydrogen of 5:1 molar hydrogen: cresol flow ratio, the catalyst lifetime increased, less byproduct is formed and the product had a better colour. The o-cresol conversion was 55% and m/p-ratio of 3.1 with 22% p-cresol selectivity was obtained when the reaction was carried out

at 380°C and 60 bar. m-Cresol was also isomerised at the same conditions and conversion of 49.7% was obtained with an o/p ratio of 1.4 and a 32.8% p-cresol selectivity. It is thus evident that higher p-cresol selectivity was obtained during m-cresol isomerisation and another point to note is the fact that a decrease in m-cresol conversion (28%) gave an increase in p-cresol selectivity (60%).

Engel and Gilson[37] (1987) have improved the isomerisation process as compared to the precedent patent by treating an acidic ZSM5 catalyst with diammoniumhydrogen phosphate. The catalyst contained 1 to 8% by weight phosphorous and the isomerisation reaction is carried out at temperatures ranging from 350-500°C, pressures of 1-60 bar, LHSV of 1-5 hr^{-1} and hydrogen was still used. The phosphorous containing catalyst was less affected by coking, thereby indicating greater stability. The highest o-cresol conversion was 41% with a m/p ratio of 3 and a p-cresol selectivity of 24%. The absence of heavies and the selectivity of 29% towards p-cresol, from an o-cresol conversion of 10%, were also reported. One of the claims, in both these patents, is that the isomerisation can be applied to m-cresol as well.

During 1991 BASF was awarded a patent for the preparation of mixtures of isomeric cresols[38] in the gas phase. The claims were for using "pentasil" type zeolite to isomerise o-cresol at 300-600°C under 0.01-50 bar. The aim was to strive for a high p/m-cresol ratio up to 10:1 in the products however; this was only attainable at conversions below 10%. The highest o-cresol conversion reported was 65% and the highest p/m selectivity 100%. The yield of by-products was <4%, even at o-cresol conversions >50%. The patent reveals that para-selective zeolites have quite large crystal diameters throughout and this was the improvement of this invention.

Further patents, during 1991 and 1993, for the isomerisation process of cresols with an improved catalyst (ZSM5) were issued to UOP[36, 39]. The catalyst consisted ideally of 11% ZSM5 that had been impregnated with less than 1% of platinum and the platinum was given a lead modifier of less than 1% as well as

an inorganic oxide binder. The platinum-bearing catalyst was tested with m-cresol in a pilot plant at 350-450°C, pressures of up to 60 bar and LHSV 1,0 hr^{-1}. The cresol equilibrium composition was taken to be 55% m-l, 23% p- and 22% o-cresol. The platinum-bearing catalyst was a more active isomerisation catalyst for m-cresol isomerisation to o- and p-cresol than the conventional ZSM5.

Imbert[40, 41] *et.al.* investigated the effect of Si/Al ratio on the transformation of m- and o-cresol over HY zeolites as well as the mechanism for m-cresol isomerisation in o- and p-cresol. Three HY zeolites samples with framework Si/Al ratios of 4.5, 16.6 and 55 were used for the isomerisation of m- and o-cresol at 380°C and atmospheric pressure in a fixed-bed reactor. HY activity in cresol isomerisation increased with increasing number of framework aluminium atoms, as expected for a reaction catalysed by Brønsted acid sites, and the observed products (isomerisation and disproportionation) were cresol, phenol and xylenols. These catalysts were rapidly deactivated and this is evident based on the weight percent of coke formed after one hour which was 12.5, 9.8 and 7.3% for HY 4.5, 16.6 and 55 respectively. The Si/Al ratio had an effect on the isomerisation selectivity and the m/p ratio was constant at 4 (HY 4.5), 1.75 (HY 16.6) and in contrast for HY (55) this ratio decreased with deactivation and the m/p-ratio was discerned to decrease with increasing Si/Al ratio.

Isomerisation via 1,2-methyl shift was the main pathway in the cresol transformation on HZSM5 and disproportionation was <0.4% at conversion of 25.7% and decreases from ortho to meta to para and increases as conversion decreases.

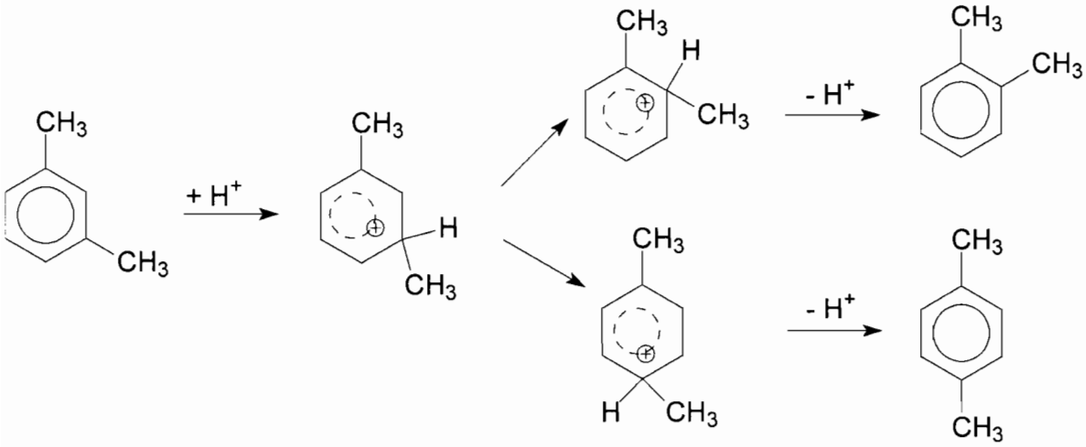
2.5.6 Basic catalyst

Dalman and Neuman[42] reported "rearrangement" and disproportionation experiments of lower ortho and para alkyl phenols in the presence of caustic at temperatures of 350 - 420°C and pressures of 136 - 340 bar. The reason for the high pressures was to enhance disproportionation and when o-cresol was isomerised, a mixture of phenol (17%), o-cresol (24%), p-cresol (9%), 2,6- and

2,4-xylenol (20 and 4% respectively) and 26% others (mostly tars) was obtained but no m-cresol was formed. When p-cresol plus phenol was reacted in a 1:5.3 ratio, a mixture of phenol (74%), o-cresol (2%), p-cresol (13%) and 11% others (mostly tars) was obtained and again neither the m-isomer nor the xylenols were formed.

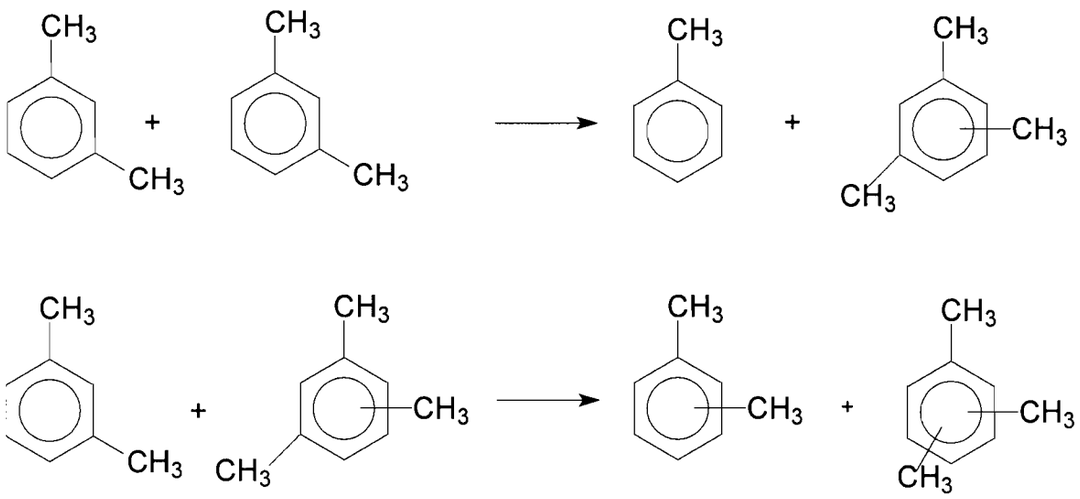
2.5.7 Mechanism of acid catalysed isomerisations

The mechanism of acid catalysed cresol isomerisation is assumed to be analogous to the xylene isomerisation mechanism. Two mechanisms for the acid catalysed isomerisation of xylene have been proposed, a unimolecular (Scheme 2.10) and bimolecurlar pathway (Scheme 2.11).



Scheme 2.10 Proposed unimolecular pathway for m-xylene

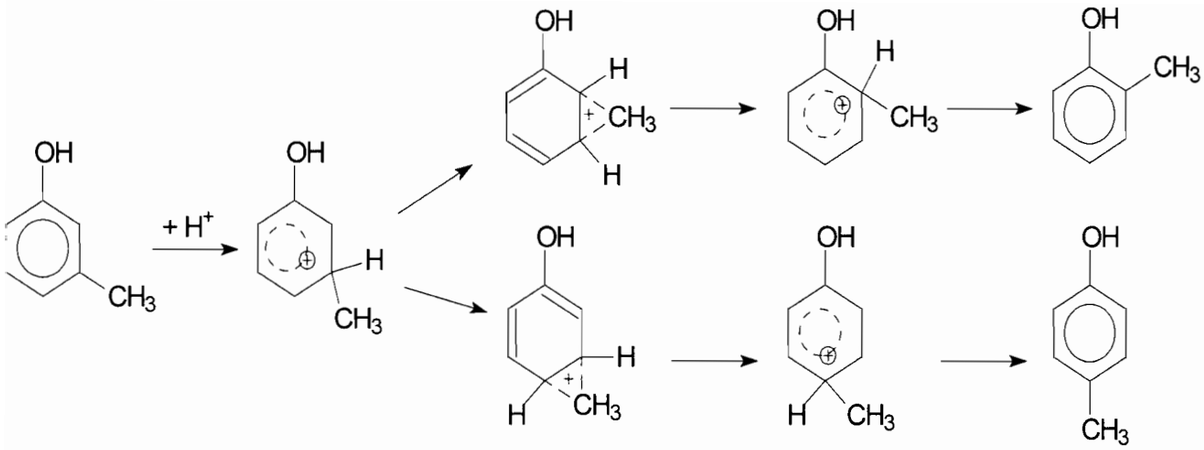
The unimolecular mechanism involves transformation of benzenium ion intermediates through a methyl shift and since this is the limiting step, no direct isomerisation of p-xylene into o-xylene (or vice versa) can occur in the absence of diffusion limitations, thus m-xylene leads to o- and p-xylene at approximately similar rates. With shape selective zeolites m-xylene is preferable transformed into p-xylene, the smallest isomer[44].



Scheme 2.11 Proposed bimolecular pathway for m-xylene

With large pore zeolites, a secondary disproportionation-transalkylation process occurs and the high rate of transalkylation renders another possible isomerisation mechanism involving successive bimolecular reaction. Through this bimolecular pathway, there is a preferential formation of o-xylene from m-xylene isomerisation.

Over medium pore zeolites such as ZSM5, or at higher temperatures isomerisation occurs unimolecularly by a 1,2-methyl shift of a protonated intermediate in sequential steps[43, 44]. Scheme 2.12 below is a proposed mechanism for m-cresol isomerisation[41]. p-Cresol diffused out of the shape selective zeolite pore much more rapidly than the more bulky o-cresol and this is consistent with the proposed mechanism for xylenes.



Scheme 2.12 Proposed mechanism for m-cresol isomerisation

Corma[45] *et.al.* did kinetic and isotopic studies on the mechanism of the catalytic isomerisation of xylenes. Over amorphous silica-alumina at high temperature and 15 bar the results indicated that the three isomers are interconverted via 1,2-shift via the consecutive reaction, e.g.

ortho → meta → para.

Isotopic studies showed that the isomerisation proceeds almost exclusively by intramolecular 1,2-shifts of the methyl groups around the ring. When using zeolite HY as catalyst more than 20% of the m- and o-xylenes, obtained from p-xylene are formed via a bimolecular transalkylation mechanism[46].

At low temperature over a large pore zeolite such as zeolite Y, the isomerisation occurs to a significant extent in a bimolecular mechanism by consecutive transalkylation steps. Imbert[41] showed that for the transformation of m- and o-cresol over HY, both xylenols and phenols are formed during the reactions. A simple qualitative indication towards the existence or non existence of the bimolecular mechanism is the formation or non formation of transalkylation products[47].

The rate ratio of transalkylation to isomerisation increases with the size of the intracrystalline zeolite cavity[48] indicating the relative contribution of the two isomerisation mechanisms.

2.5.8 Equilibrium ratios of the cresol isomers

Table 2.2 Cresol isomer equilibrium ratios expressed as a function of temperature

	Temperature (°C)			
	Calculated			Measured
Isomer	250[a]	350[a]	380[b]	380[c]
o-cresol	0.21	0.23	0.37	0.36
m-cresol	0.72	0.68	0.58	0.48
p-cresol	0.08	0.09	0.05	0.16

a) = Equilibrium ratio calculated using ASPEN
b = Equilibrium ratio calculated using data from Stull et al.49
c = Experimental equilibrium ratios as reported by Imbert et al.41 and Fritsch et al.50

Contradictory data are presented, in literature, on thermodynamic properties and equilibrium distribution of cresols.

As discussed in section 2.5.2, "equilibrium distributions" obtained from conversion over Friedel-Crafts catalyst are inconsistent. Equilibria calculated from thermodynamic properties given by Stull et al.[49] and ASPEN result in significant differences compared to recent experimental data, obtained over solid acid catalysts (zeolites), by Imbert et al.41 and Fritsch et al.[50] see figure 2.1.

2.6 Separation of cresol mixtures

2.6.1 Chemical and physicochemical properties of cresols

Pure o- and p-cresol are crystalline solids while m-cresol is a viscous oil at room temperature. The cresols have a phenolic odour and are colourless but become yellow to brown after some time.

Cresols are very corrosive and at elevated temperature unalloyed steel is attacked by cresols to a noticeable extent and the severity of the attack are dependent on the water content. Aluminium and its alloys are attacked severely, at temperatures >120°C, when the water content of the cresol is too low and when it is <0.3%, corrosion may proceed explosively. The corrosive behaviour of cresols can alter significantly, depending on the presence of other compounds, and the simultaneous presence of water soluble chlorides and basic nitrogen containing compounds can lead to very severe corrosion of stainless steel.

The solubility of the cresols in phenol and in many organic solvents, i.e. aliphatic alcohols, ethers and chloroform, is high but they are less soluble in water than phenol. The presence of other water-soluble organic compounds (e.g. methanol) raises cresols solubility in water and reduces the critical solution temperature while dissolved inorganic salts lower the water solubility of cresols.

Cresols form azeotropes with a number of compounds such as decane and ethylene glycol and it can be distilled with steam.

The cresols are chemically similar to phenol and they are weak acids and dissolve in aqueous alkali to form water stable salts known as cresolates. They can be extracted into sodium hydroxide solution from solvents that are not miscible with water.

The hydroxyl group is accessible for further conversion and etherification as well as esterification of the hydroxyl group is possible as well as the formation of urethanes when isocyanates react with the hydroxyl group. Under drastic conditions (420°C, Al_2O_3), the hydroxyl group is replaced by ammonia and the corresponding toluidine is obtained.

Hydrogenation can target the aromatic nucleus or the hydroxyl group and in the vapour phase (300-400°C and ~8 MPa), in the presence of catalysts containing transition metals and aluminium oxide, gives toluene. Methylcyclohexanols or methylcyclohexanones are formed when hydrogenation is performed over a

stirrer and a dip tube, fitted with a micron frit. A bursting disk was also present in case of excess pressure.

4.1.3 Catalyst calcination

Raney nickel or noble-metal catalyst and hydrodealkylation occurs at 500-700°C where cresol is demethylated to phenol.

Cresols are very sensitive to oxidation and depending on the oxidising agent, conditions and position of the methyl group, oxidative reactions lead to a number of compounds such as hydroquinones, quinines and cyclic ketones. After protection of the hydroxyl group by esterification or etherification, the methyl group can be selectively oxidised to a formyl group (i.e. with manganese dioxide or oxygen) or to a carboxyl group (with acid permanganate solution). Alkali fusion of the cresols in the presence of lead oxide or manganese dioxide produces the corresponding hydroxybenzoic acids directly.

Cresols readily undergo electrophilic substitution on the ring and nitrosation, halogenation, sulfonation and alkylation occur readily[1].

2.6.2 Separation of cresol mixtures

The following is a brief discussion of some of the separation techniques used for separating cresol mixtures.

2.6.2.1 Distillation

The boiling points of o-, m- and p-cresol are 191.0°C, 202.2°C and 201.9°C respectively. Only o-cresol can be separated as a pure product by distillation from mixtures of the three cresol isomers. m- and p-Cresol are obtained as a single fraction because the difference between their boiling points is too small for separation by distillation, even when carried out under vacuum. The separation of m/p-cresol mixtures by azeotropic distillation with benzyl alcohol or by countercurrent extraction with selective solvents has acquired no practical importance industrially. The dissociative extraction and distillation processes, that exploit the higher dissociation constant (higher acidity), of m-cresol in relation to that of p-cresol has also found no industrial application[1].

2.6.2.2 Crystallization

The melting points of o-, m- and p-cresol are 31.0°C, 12.2°C and 34.7°C respectively. Crystallisation is of practical importance as a technique for the separation of pure p-cresol from m/p-cresol mixtures of high p-cresol content. Until now, this method has generally been carried out at normal pressure. Kobe Steel, in Japan, has recently developed a high-pressure crystallisation technique known as the Finecry process for industrial use[1].

2.6.2.3 Adsorption

p-Cresol adsorbs more strongly than m-cresol on an alkali metal or alkaline earth metal modified zeolite of e.g. type X or L, or ZSM5 as well as titanium dioxide. m/p-Cresol mixtures can therefore be separated in an adsorption column and desorbed again with a suitable desorbent like an aliphatic alcohol or a ketone. UOP developed a continuous version of this process which is known as the Cresex process and is analogous to its industrially used Parex and Forbex process family. Merisol uses this process industrially in the United States. One isomer, either m- or p-cresol, can be isolated at a purity of 99% in a single operation (single column) while the purity of the other isomer obtained is only 91%[1].

2.6.2.4 Separation via addition compounds

Many organic nitrogen compounds react with m- or p-cresol to form crystalline addition compounds that can be separated from the reaction mixture. These addition compounds can be decomposed to regenerate the nitrogen compound and the respective cresol isomer. Benzylamine, for example, forms a 1:1 adduct with m-cresol, which has a melting point of 39.5°C. The adduct is centrifuged and fractionated by distillation and pure m-cresol is obtained. Pure p-cresol is isolated by crystallization from the mother liquor.

Another process of industrial importance is the isolation of m-cresol via a 1:1 addition complex with urea.

Advantage may be taken of adduct formation between cresols and phenol or certain phenol derivatives with a view to effecting separation. For example, m-cresol forms an adduct with phenol with a melting point of 25.9°C, while p-cresol forms an adduct with bisphenol A [isopropylidenedi(p-phenol)].

m-Cresol can also be precipitated from m/p-cresol mixtures as an addition compound with anhydrous sodium acetate in an organic solvent, i.e. toluene or benzene, at 20-40°C. The precipitate is removed from the mother liquor and decomposed in the same solvent by heating to 80-95°C and m-cresol stays in solution while sodium acetate remains as a solid. m-Cresol is obtained from the organic solvent as a product (96-99%)[1] of technical purity.

2.6.2.5 Separation via ester or salt formation

The mother liquor enriched with p-cresol (i.e. to a m/p ratio of 35:65), from the precipitation with sodium acetate, can react with oxalic acid to give the mono or diester. This ester is precipitated on cooling to 20°C, separated and then hydrolysed by heating with water in the presence of a nonpolar organic solvent. The p-cresol dissolves in the solvent from which it is isolated by distillation. The oxalic acid is precipitated from the solvent upon cooling and recycled.

The alternating use of both processes, sodium acetate precipitation of m-cresol and ester precipitation of p-cresol, separates m- and p-cresol almost entirely.

Separation of the cresols via the calcium cresolates, in which advantage is taken, either of the relative greater solubility of the calcium p-cresolate or of the easier hydrolysability of the m-cresolate with superheated steam, is unsatisfactory or has no practical use industrially[1].

2.6.2.6 Separation by nuclear substitution

A large-scale industrial process used by Sumitomo in Japan and Bayer in Germany comprises the separation of m- and p-cresol via the di-*tert*-butyl derivatives. In this technique, the m/p-cresol mixture reacts with up to 2 moles of

isobutene per mole of cresol in the presence of acidic catalysts (sulphuric acid). The resulting alkylated products, mainly 2,6-di-*tert*-butyl-p-cresol and 2,4-di-*tert*-butyl-m-cresol, with boiling points at 2.67 kPa of 147°C and 167°C respectively allows for easy separation by vacuum distillation. The process also yields monobutylated cresols, which can be returned to the alkylation reactor and pure m- or p-cresol and isobutene are subsequently recovered by dealkylation of the di-*tert*-butylcresols in the presence of the acidic catalyst. The individual cresols are then further purified by distillation. The butylation-debutylation process is attractive, not simply because it gives a very high yield of pure cresol isomers, but also because it enables 2,6-di-*tert*-butyl-p-cresol, a widely used antioxidant BHT, to be produced simultaneously[1].

3. OBJECTIVES OF THIS STUDY

In order to add flexibility to the Merisol product distribution and increase the profitability of the business unit, the isomerisation of cresols was investigated during this study (Scheme 3.1)

Based on the preceding literature three commercially available zeolites (HZSM5, HBeta and HMordenite) were identified to be investigated during this study. HZSM5 is the most frequently used zeolite for cresol isomerisation and no publications appear in open literature with regards to cresol isomerisation over HBeta and HMordenite, hence the choice.

The objectives of this study thus were as follows:

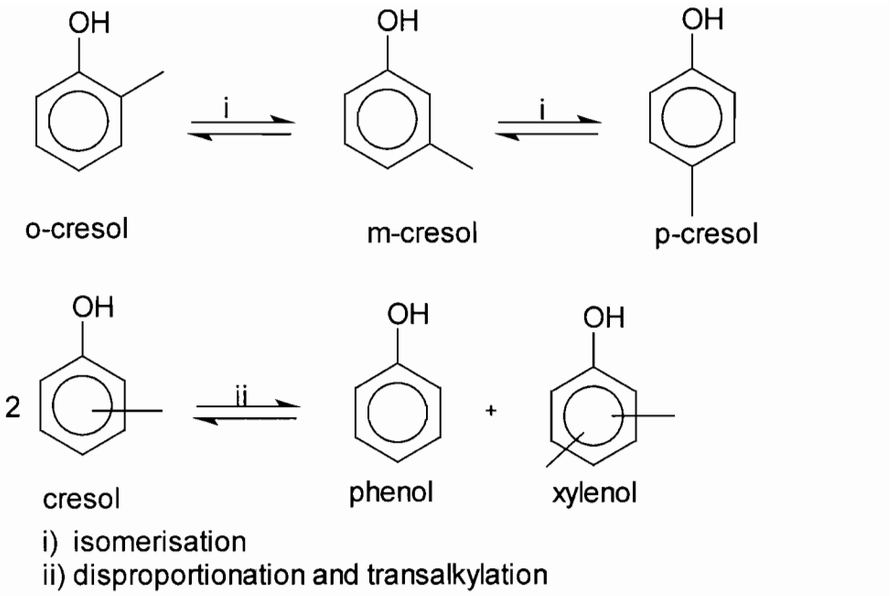
Find the best catalyst with respect to

- Activity
- High selectivity towards isomerisation (i.e. low selectivity towards disproportionation)
- High stability (i.e. low deactivation/coking tendency)

In order to achieve these objectives, experiments were carried out as follows:

i) Batch-wise liquid phase screening of acid zeolite catalysts (HZSM5, HBeta and HMordenite) with regards to cresol isomerisation and disproportionation.

ii) Vapour phase evaluation of o-cresol isomerisation over HZSM5, HBeta and HMordenite catalysts towards time-on-stream operation as to stability.



Scheme 3.1 Reaction scheme for cresol isomerisation over zeolites

4. Experimental

Experiments were carried out in the liquid phase, batch-wise mode, as well as in the vapour phase, continuous mode.

The cresol isomers were used without further purification. The m- and p- cresol was purchased from Aldrich and the o-cresol from Sasol and the purity of all the cresol isomers were >99 %.

The zeolites (HZSM5, HBeta and HMordenite) were purchased from Süd Chemie. The zeolites were applied in the powder form (< 100 micron) and the SiO_2/Al_3O_2 ratio was 90, 50 and 80 for HZSM5, HBeta and HMordenite respectively. This information was received from the supplier of the zeolites.

4.1 Batch-wise liquid phase experimentation

4.1.1 Storage facilities and handling of reagents

The cresol and zeolites, as well as the autoclave were placed into the glove bag with a scale inside. A vacuum pump, and allowing the argon to flow in, was connected to the glove bag because an inert atmosphere had to be created every time the glove bag was used. Evacuating the glove bag with the vacuum pump and allowing the argon to flow in, created the desired inert atmosphere. To ensure all the air was removed from the glove bag, the procedure was repeated at least three times.

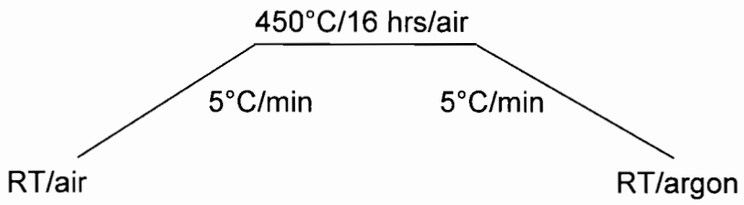
4.1.2 Reactor

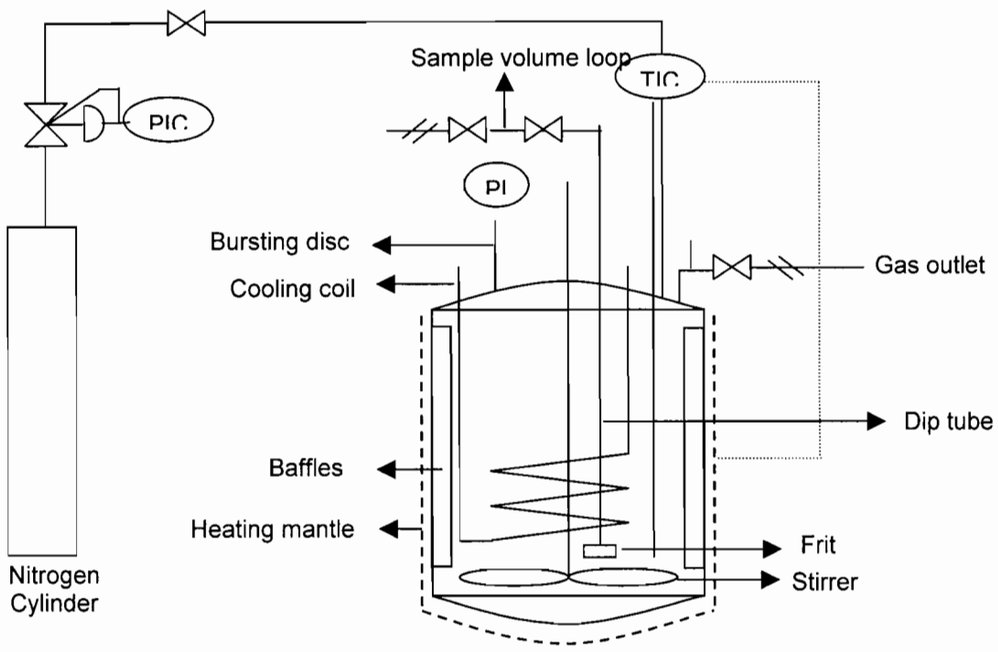
The liquid phase isomerisation was performed in a 300ml autoclave (Scheme 4.1) manufactured by the PARR company. The inner diameter of the autoclave was 5.8cm and the length 11.5cm. This autoclave was equipped with a heating mantle, gas in- and outlet, cooling coil (safety precaution in case of a runaway reaction), temperature control and indicator and pressure indicators, mechanical

stirrer and a dip tube, fitted with a micron frit. A bursting disk was also present in case of excess pressure.

4.1.3 Catalyst calcination

Calcination is necessary to activate the zeolites already in the hydrogen form. Since *in situ* calcination was not an option in the autoclave, a calcination oven was utilised for this purpose. The calcination was done in a 50cm quartz tube (inner diameter of 2cm), of which 25cm was in the oven, and 25g of zeolite was used per charge. The amount of zeolite calcined was just enough for one reaction and every time a fresh batch needed to be calcined. The calcination was performed under an air flow and argon was used during the cooling step. The zeolite was removed under argon and placed into the glove bag. This procedure was necessary because the zeolites are very hygroscopic once calcined. All the calcinations were done overnight and the following temperature programme was employed:





Scheme 4.1: 300ml autoclave set-up for batch-wise liquid phase isomerisation

4.1.4 Reaction set-up

Table 4.1 The operating conditions for the liquid phase reactions:

	Charging reactor	Operating reactor
Temperature (°C)	25	250
Total pressure (bara)	15 (N_2)	ca. 30*
Partial pressure of cresol (bar)	-	2.7 – 3.5**
Percentage of total cresol being in vapour phase	-	9 – 12**
Stirring rate (rpm)	-	1500

* Pressure drop during operation due to repeated sampling was ca. 2 bar.
** Calculated

43.5g of cresol, along with 20g of the zeolite catalyst, were placed into the autoclave inside the glove bag. The autoclave was sealed inside the glove bag and nitrogen (charged to the reactor outside the glove bag) pressed in until an initial operating pressure of 15 barg was reached (the final reaction pressure was not noted). The autoclave was gradually heated to 250°C and maintained at this temperature. The initial heating rate was fast but from 240°C to 250°C about fifteen minutes was necessary to reach the final operating temperature. Since the heating mode is electrical, the temperature will overshoot the set point by about 5°C before stabilizing at 250°C. Samples were taken at different time intervals (see Section 4.1.5). All the samples drawn as well as the final reaction mixture, after cooling to room temperature and depressurising, were subjected to gas chromatographic analysis.

This procedure was repeated for all the cresol isomers and zeolites under investigation.

4.1.5 Sampling

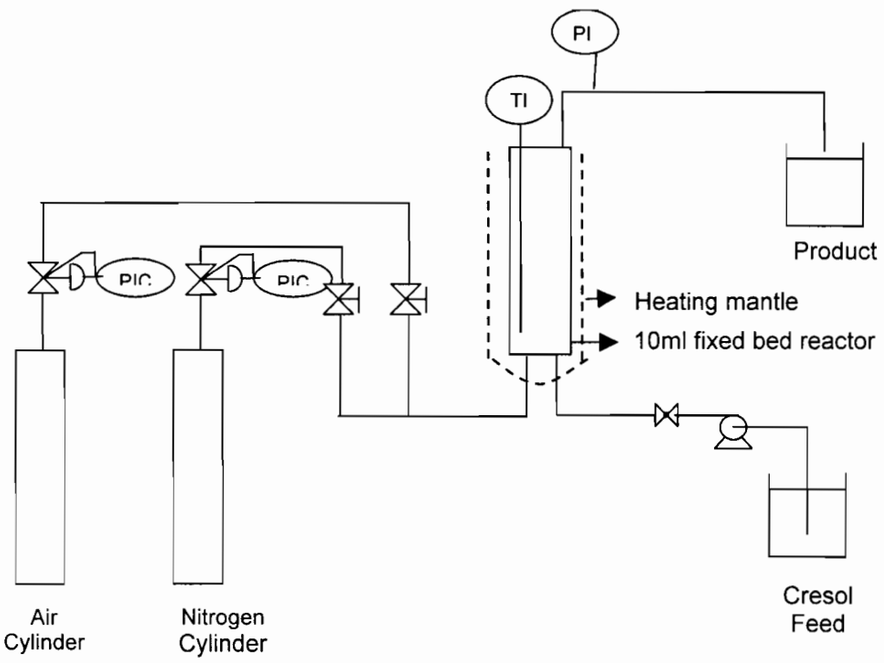
The reactor was equipped with a 0.125-inch dip tube, fitted with a 2-micron frit and two ball valves. The two valves were needed for filling the sample loop with sample and discharging the sample into a vial. Ball valve two (closest to the sample point) is closed when ball valve one (closest to the autoclave) is opened and visa versa. A frit was used to prevent catalyst losses during sampling. Before each sample for analysis, flushing of the sample loop occurred to ensure a representative sample is drawn. A sample (between 0.2-0.6g) was taken at time intervals between 30-60 minutes. Due to the fact that reaction started to occur at about 240°C (see section 4.1.4), the first sample is already mixed with product that formed during that 10°C increase to the operating temperature.

4.2 Vapour phase experimentation

4.2.1 Reactor

Gases (air and nitrogen) with pressure regulators and needle valves formed part of the set-up (Scheme 4.2). The fixed-bed reactor consists of a 10ml catalyst bed, inner diameter of 1cm, length of preheating section 10ml and the entire length of the tube 40cm. This was equipped with a heating jacket, temperature control and indicator and pressure control and indicator. An HPLC pump, to feed the reagents and a product-collecting vessel was also incorporated. Quarter inch tubing was utilised for the construction of the experimental set-up. The entire set-up was constructed in a fume hood for safety reasons.

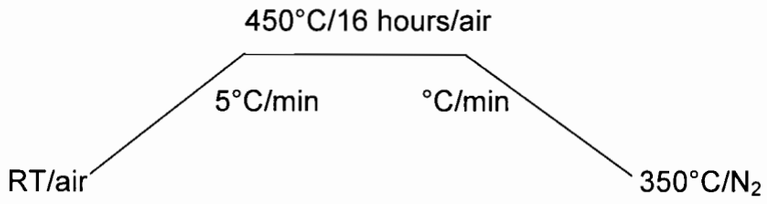
The fixed-bed reactor was equipped with a preheating section, filled with glass beads. This section was needed to evaporate and preheat the o-cresol to the operating temperature for the isomerisation to occur immediately.



Scheme 4.2: 10ml fixed bed reactor set-up for continuous flow vapour phase isomerisation

4.2.2 Catalyst calcination

The undiluted zeolite (10ml) was loaded and an *in situ* calcination performed. The temperature program employed follows below.



The calcination was performed overnight at 450°C, under air. Upon cooling to the operating temperature, a nitrogen flow was maintained.

4.2.3 Reaction set-up

Table 4.2 The operating conditions for the vapour phase reactions:

Temperature (°C)	350
Total pressure (bara)	2
Feed partial pressure (bar)	1.64*
LHSV (hr^{-1})	1**
Pump rate (ml/min)	0.17

* Considering 3.5wt% (= 18mol%) of moisture
** Moist feed

The o-cresol was mixed with 3.5wt% distilled water and fed to the reactor at 0.17ml/min to maintain a LHSV of 1.02hr^{-1}. Water is added because o-cresol is a solid at room temperature. Water will reduce the rate of reaction by reducing the partial pressure of cresol (refer to table 4.2). Chemical inhibition by moisture

content in the percent range (wt) has not been observed during similar reactions over acid zeolite catalysts (Walter Böhringer, Catalysis Research Unit, Department of Chemical Engineering, UCT, personal communication) and water content of 3.5wt% had no effect on the catalyst lifetime (Trey Clanton, Merisol Houston, USA, personal communication)."

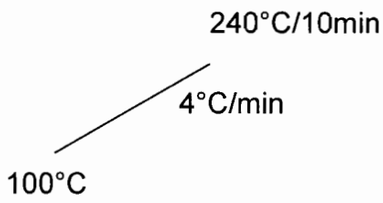
4.2.4 Sampling

The first sample droplets were observed after two hours. The product condenses in the line to the product vessel. The approximate volume of the tube from the reactor to the product vessel was 20 ml and it corresponds to a mean residence time of 2 hours of the condensed product in this line, at the given pump rate. The effect of residence time and back mixing in the line could be ignored because the duration of the experiment with the stable zeolite catalysts, was about one week. The frequency of the sampling was 3 ~~times/day except~~ for HZSM5 that was once/day as from the second day on stream.

4.3 Analysis

Samples were obtained in the liquid form and a gas chromatography (GC) method was developed for the analysis of the reaction mixture.

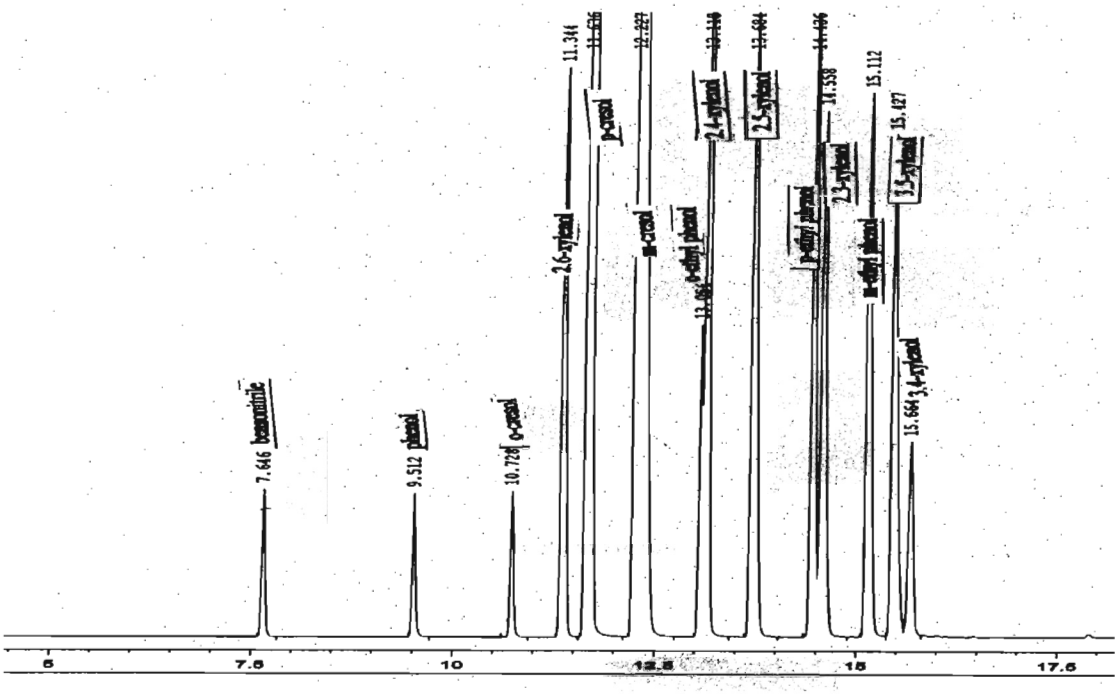
An Alpha Dex column was purchased from Supelco with dimensions of 30m x 0.25mm x 0.25µm-film thickness Fused Silica Capillary Column. A Hewlett Packard HP 6890 GC instrument fitted with an auto sampler was utilised. The following temperature programme was employed:



The conditions for the GC were as follows (FID):

Auto inject (µl)	0.2
Split	183
Injector pressure (psig)	11.5

A GC of a standard mixture is presented in Scheme 4.3.



Scheme 4.3 GC of a standard cresylic acid mixture

4.3.1 FID response factors

FID response factors (Table 4.1) were determined in-house. A standard mixture, containing all C_6 – C_8 phenols as well as benzonitrile, was prepared. The benzonitrile was included because it is an impurity in the phenolic feed stream. The exact mass of each compound was noted and hence the mass percent was calculated.

Preliminary response factors were obtained from Sasol Chemical Industries (SCI) routine GC analysis laboratory and used as a reference/starting point for the calibration of the GC. The standard mixture was injected on the GC and a

preliminary mass distribution was calculated, using the response factors obtained from the routine laboratory (equation 1). The individual response factors were manipulated until the calculated mass distribution of the phenols matched the composition of the standard mixture (Table 4.3). The standard mixture was injected ten times to ensure reproducible results and regular injection of the standard mixture was performed during the course of the investigation.

$$\text{Mass fraction} = \frac{\text{Peak area}_i \ / \ \text{Response factor}_i}{\sum_j \text{Peak area}_j \ / \ \text{Response factor}_j} \qquad (1)$$

Table 4.3 FID Response factors determined and used for the data evaluation

Compound	RF (determined)
Phenol	0.68
o-Cresol	0.68
2,6-Xylenol	0.74
p-Cresol	0.55
m-Cresol	0.64
2,4-Xylenol	0.71
2,5-Xylenol	0.70
2,3-Xylenol	0.70
3,5-Xylenol	0.67
3,4-Xylenol	0.64

4.4 Data evaluation

The following definitions and equations were used for the evaluation of the data obtained.

4.4.1 Conversion

The conversion was calculated based on the amount of unreacted starting cresol.

$$\text{Conversion (X)} = 1 - \text{mass fraction unreacted cresol} \qquad (2)$$

4.4.2 Isomerisation selectivity

The selectivity was based on the isomerised cresols, for instance, starting with o-cresol then the isomerisation selectivity will be given as the sum of m- and p-cresol divided by the conversion. Depending on the starting cresol isomer, the sum of yields of the isomerised cresols was taken to express an isomerisation selectivity according to

$$S = Y / X$$

Calculation was done on mass basis (see equation 1) so that

$$S_{\text{isomerisation}} = Y_{\text{isomerised cresol}} / X_{\text{feed cresol}}$$

For e.g. o-cresol isomerisation:

$$S_{\text{isomerisation}} = (Y_{\text{m-cresol}} + Y_{\text{p-cresol}}) / X_{\text{o-cresol}} \quad (3)$$

4.4.3 Disproportionation selectivity

The disproportionation selectivity was based analogously on the amount of phenol, xylenols and higher alkylated phenols formed.

$$S_{\text{disproportionation}} = (Y_{\text{phenol}} + Y_{\text{xylenols}}) / X_{\text{o-cresol}} \quad (4)$$

4.4.4 Activity

Activity was expressed as relative activity to give some semi-quantitative interpretation of the differences between catalyst samples and the data obtained was not suitable to do a serious kinetic (i.e. activity) analysis.

Activity = (slope x mass cresol) / mass catalyst (5)

5. RESULTS

Experience in the group on other phenolic conversion reactions carried out in the used autoclave reactor, showed that the equipment was very reliable so that there was no need to carry out another blank run in order to check for wall catalysed or thermal reactions.

Experience in the group on conversion of phenolic compounds in stainless steel fixed bed reactors under similar reactor conditions, shows that the extent of thermal reactions and reactions catalysed by the reactor wall or the catalyst diluent/preheating packing material (glass beads) is irrelevant as well.

5.1 Batch-wise liquid phase isomerisation

Since isomerisation of cresol is almost always accompanied by disproportionation to the same extent, the aim of this part of the dissertation was to investigate isomerisation vs. disproportionation for the three cresol isomers (o-, m- and p-cresol) during batch-wise transformation over zeolites HZSM5, HBeta and HMordenite.

Due to the lack of data in the low conversion range (up to 5%) from most of the experiments and the significant scatter of the low conversion data points, a sound conventional kinetic evaluation following the method of initial rates, could not be performed. Data at higher conversion were susceptible to catalyst deactivation and, in the case of m-cresol feed, approach to thermodynamic equilibrium conversion so that a kinetic analysis including higher conversion data, was also not possible. Despite these drawbacks, an attempt was made to quantify catalyst activity by approximating the method of initial rates using trendlines which were determined as lines through the origin and the first few low to medium conversion data points. The slopes of these trendlines (somehow averaging the scatter of data) are used as a rough estimate to compare catalyst activities. Results are given in tables 6.1 - 6.3 and summarised in new section 6.1.4.1.

5.1.1 o-Cresol conversion

5.1.1.1 o-Cresol conversion over zeolite HZSM5

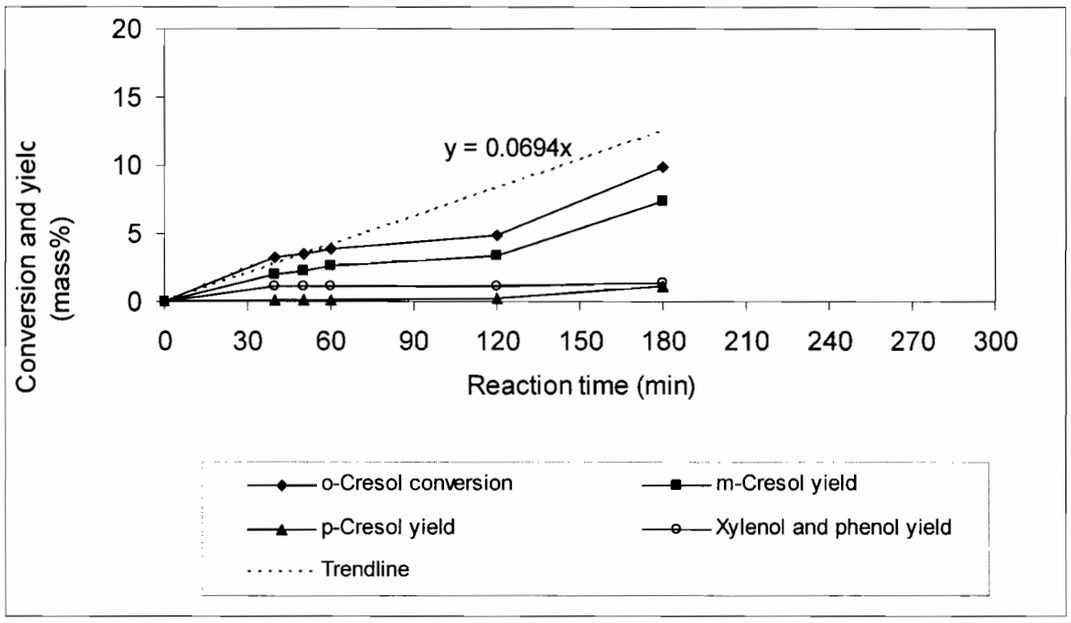


Figure 5.1: Conversion of o-cresol and yield of products, m- and p-cresol and phenol and xylenols, obtained over HZSM5 as a function of reaction time at 250°C during the batch-wise liquid phase o-cresol isomerisation in an autoclave reactor.

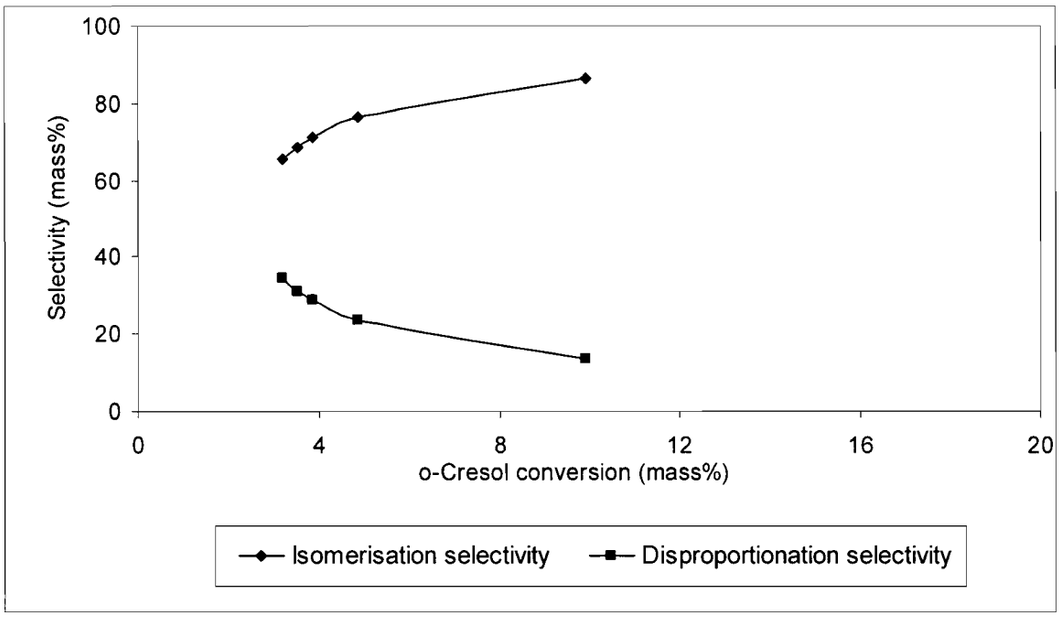


Figure 5.2: Reaction selectivity as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HZSM5 at 250°C in an autoclave reactor.

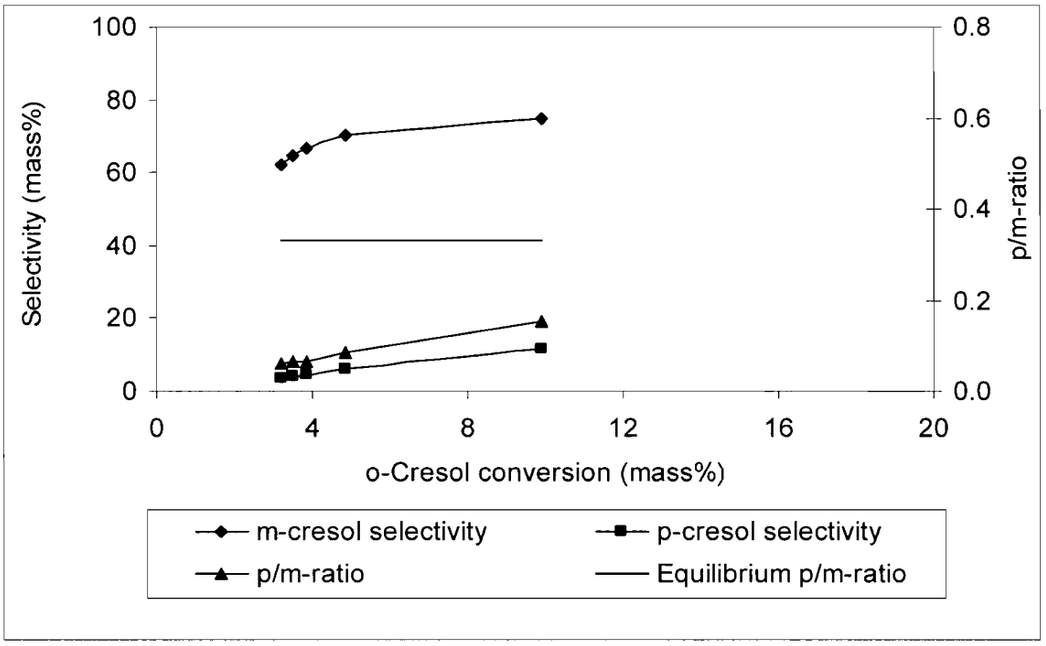


Figure 5.3: Selectivity for m- and p-cresol as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HZSM5 at 250°C in an autoclave reactor.

Figure 5.1 shows the conversion of o-cresol and yield of major products as a function of reaction time over HZSM5. The major product proved to be m-cresol followed by xylenol and phenol with p-cresol being formed in the lowest yield. While a constant xylenol and phenol content was maintained over the reaction period, m- and p-cresol concentration in the reaction mixture increased, albeit only slightly for p-cresol. Increasing conversion leads to an increase in isomerisation with a corresponding decrease in disproportionation (Figure 5.2) and it was also noted that the selectivity towards m- and p-cresol also showed an increase with increasing conversion (Figure 5.3), but the selectivity towards m-cresol remains higher than for p-cresol.

5.1.1.2 o-Cresol conversion over zeolite HBeta

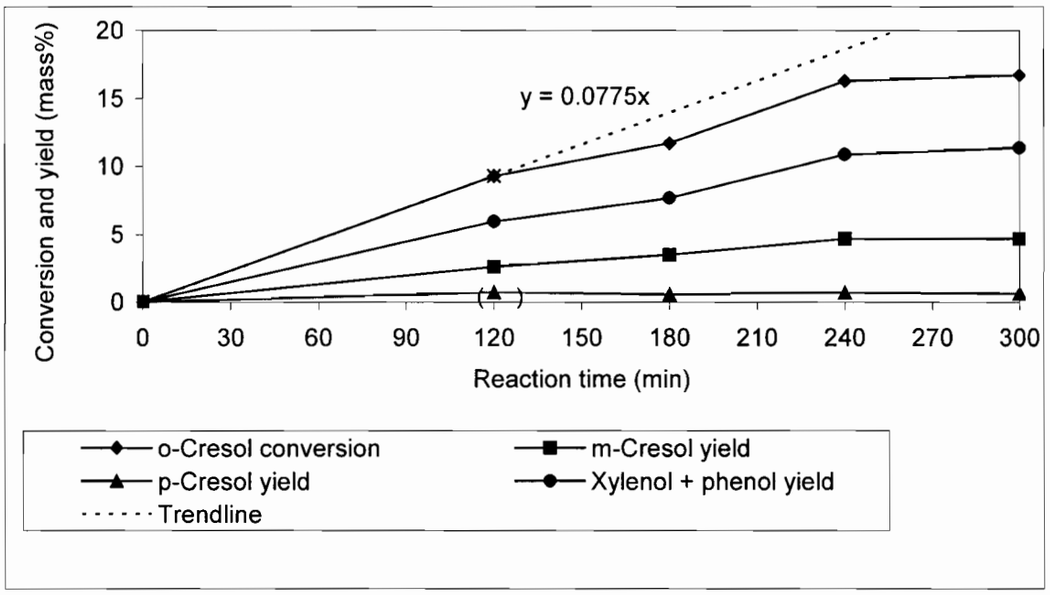


Figure 5.4: Conversion of o-cresol and yield of products, m- and p-cresol and phenol and xylenols, obtained over HBeta as a function of reaction time at 250°C during the batch-wise liquid phase o-cresol isomerisation in an autoclave reactor.

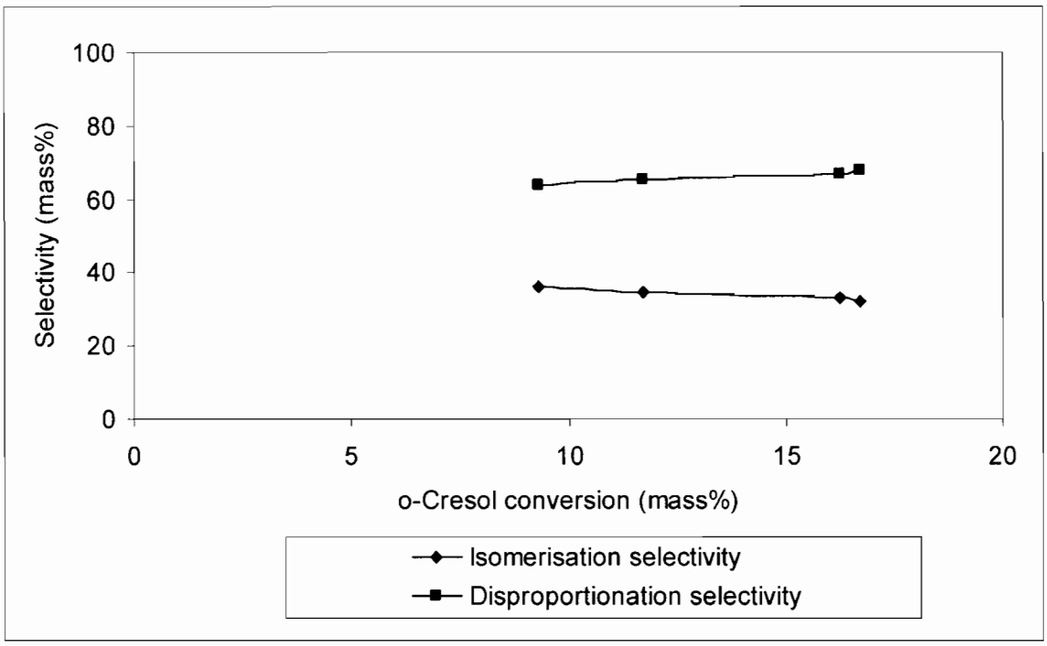


Figure 5.5: Reaction selectivity as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

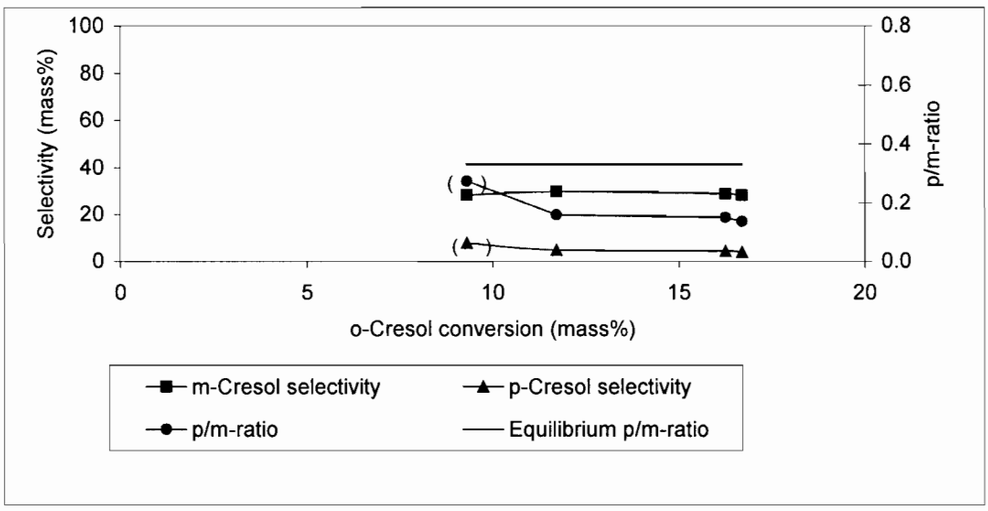


Figure 5.6: Selectivity for m- and p-cresol as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

In contrast to the reaction over HZSM5, the conversion and yields of major products for the isomerisation of o-cresol over HBeta (Figure 5.4) indicated xylenol and phenol to be the major products in this transformation. While reaction towards m-cresol remained high, virtually no p-cresol was formed. An increase in m-cresol formation with an even higher increase in xylenol and phenol content was observed over time while a constant curve was maintained for p-cresol for the duration of the reaction. Higher, but approximately constant disproportionation selectivity (Figure 5.5) was obtained with increasing conversion, while the isomerisation selectivity remained the same. While m-cresol selectivity remains more or less the same with increasing conversion (Figure 5.6), p-cresol selectivity seems to declines significantly (though on very low level). Consequently a sharp decline in the initially high p/m-ratio was observed between conversions of 9 and 12%. However, it appears from figure 5.4 that the first data point on p-cresol yield is an outlier due to experimental scatter, so that the first data points for p-cresol selectivity and p/m-ratio in figure 5.6 appear as outliers as well (data points set in brackets). At higher conversion, p-cresol selectivity and p/m-ratio remain constant at low level. The outlying data points were put in brackets (Figures 5.4 and 5.6)

5.1.1.3 o-Cresol conversion over zeolite HMordenite

Most of the reactions were performed in an autoclave that was used previously for other phenol conversion reactions and was found to be a very reliable system.

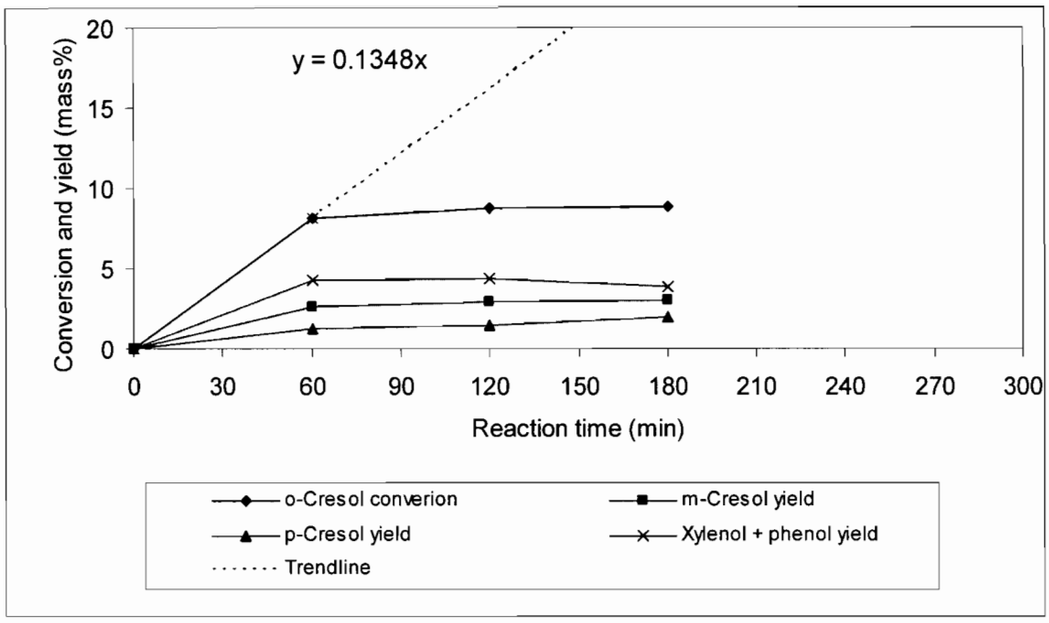


Figure 5.7: Conversion of o-cresol and yield of products, m- and p-cresol and phenol and xylenols, obtained over HMordenite as a function of reaction time at 250°C during the batch-wise liquid phase o-cresol isomerisation in an autoclave reactor.

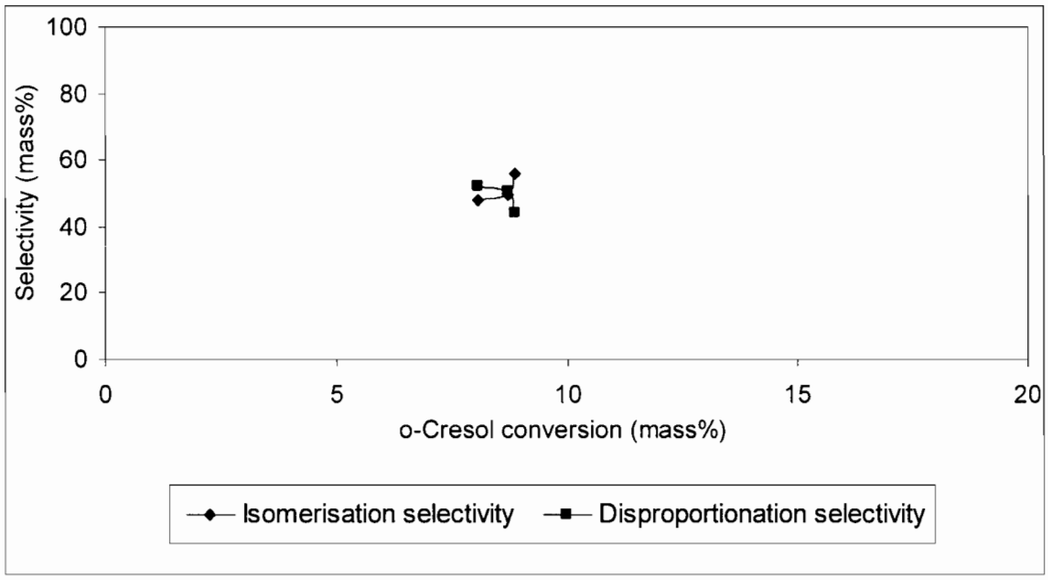


Figure 5.8: Reaction selectivity as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HMordenite at 250°C in an autoclave reactor.

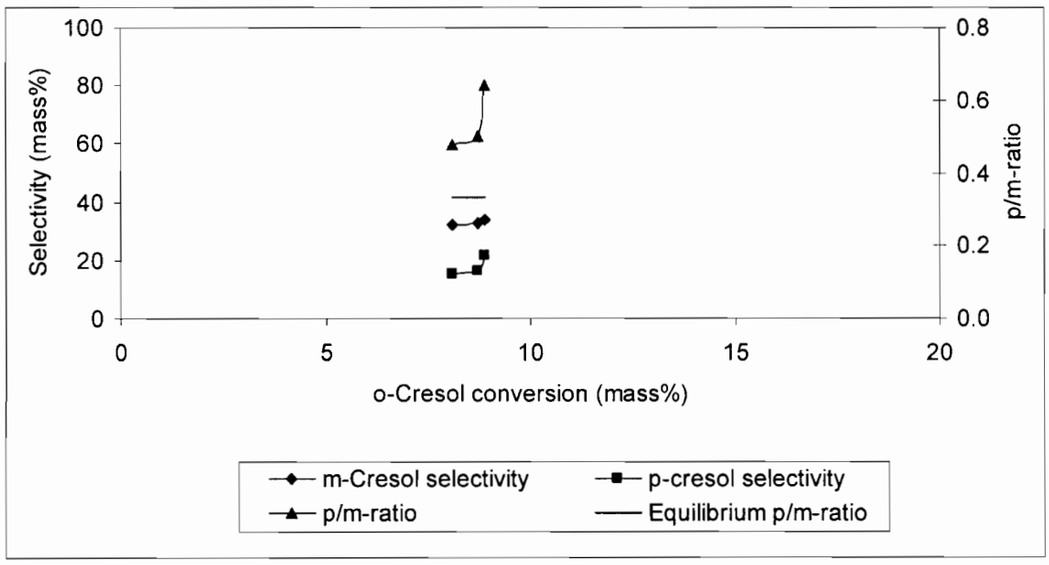


Figure 5.9: Selectivity for m- and p-cresol as a function of conversion during the batch-wise liquid phase o-cresol isomerisation over HMordenite at 250°C in an autoclave reactor.

After the initial increase in o-cresol conversion (first 60 minutes) the conversion (8.7%) remained almost the same, with expected constant yields for m-cresol, xylenol and phenol, over HMordenite (Figure 5.7). Despite differences being small, the initial higher disproportionation selectivity was replaced at higher conversion by a tendency towards increased isomerisation (Figure 5.8). Increased p- and constant m-cresol selectivity over increased conversion (Figure 5.9) led to an increase in p/m-ratio, which for the first time also proved to be higher than the equilibrium value.

5.1.2 m-Cresol conversion

m-Cresol was evaluated under the same isomerisation conditions as described for o-cresol.

5.1.2.1 m-Cresol conversion over zeolite HZSM5

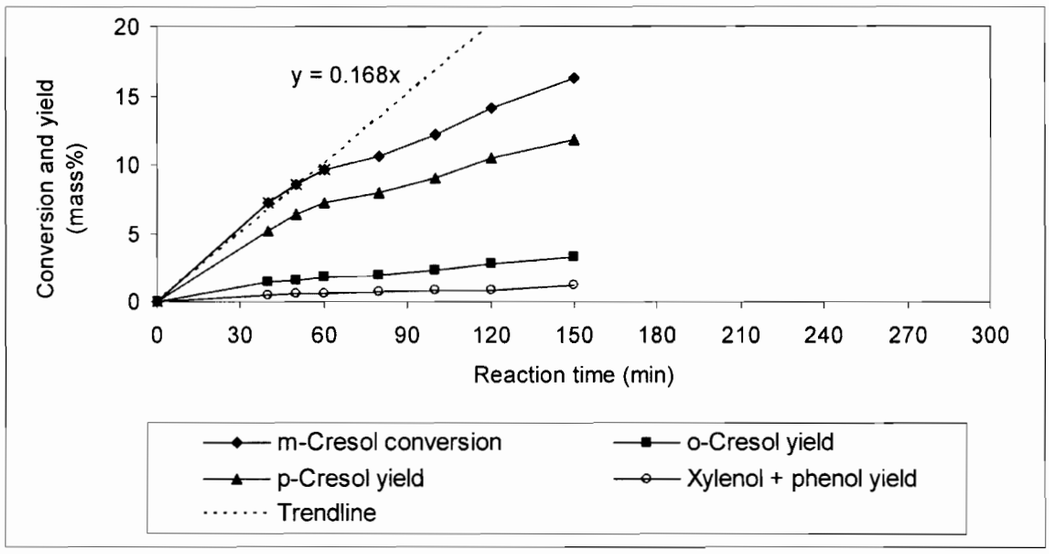


Figure 5.10: Conversion of m-cresol and yield products, o- and p-cresol and phenol and xylenols, obtained over HZSM5 as a function of reaction time at 250°C during the batch-wise liquid phase m-cresol isomerisation in an autoclave reactor.

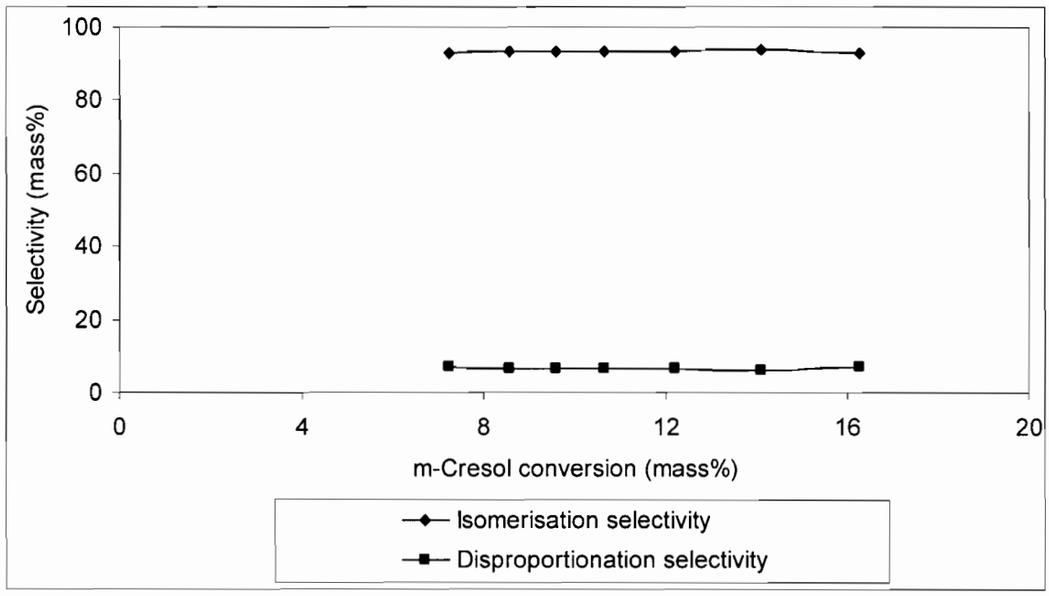


Figure 5.11: Reaction selectivity as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HZSM5 at 250°C in an autoclave reactor.

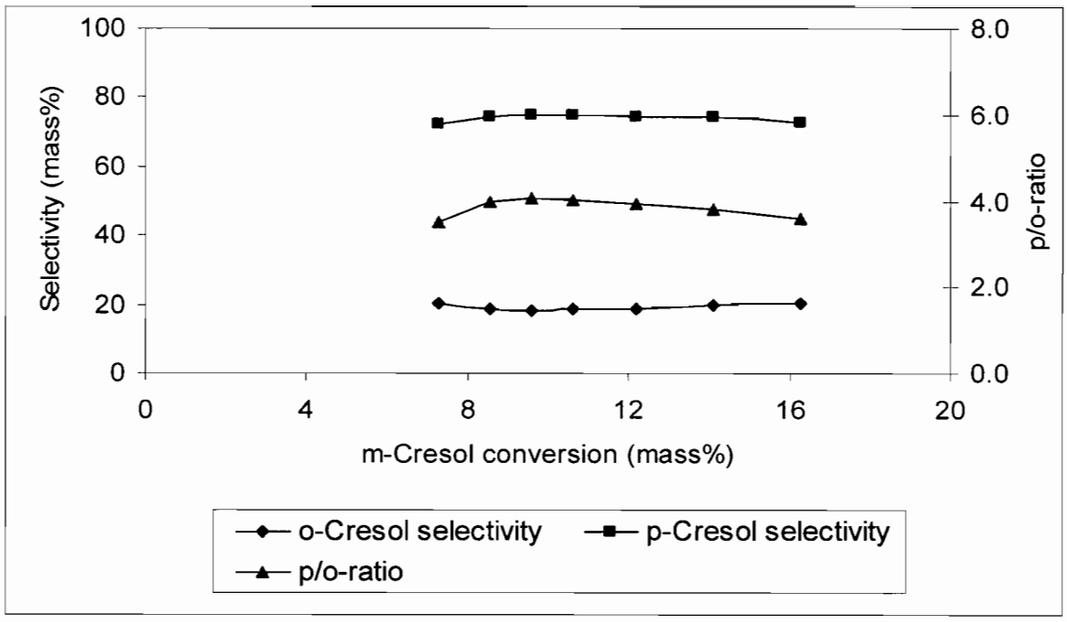


Figure 5.12: Selectivity for o- and p-cresol as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HZSM5 at 250°C in an autoclave reactor.

The conversion for m-cresol isomerisation over HZSM5 and the yield of major products is depicted in Figure 5.10 as a function of reaction time. The major product proved to be p-cresol followed by o-cresol with xylenols and phenol in lowest yield. Yields of o- and p-cresol, as well as xylenols and phenol, increased constantly with increasing conversion, though on very low levels. A high and steady isomerisation was maintained while very low disproportionation was observed with increasing m-cresol conversion (Figure 5.11). It was also discernable (Figure 5.12) that a low o- and a high p-cresol selectivity was maintained throughout the reaction and this resulted in a high p/o-ratio. An initial increase in p/o-ratio (between conversion of 7 and 10%) was observed but decreased with increasing conversion.

5.1.2.2 m-Cresol conversion over zeolite HBeta

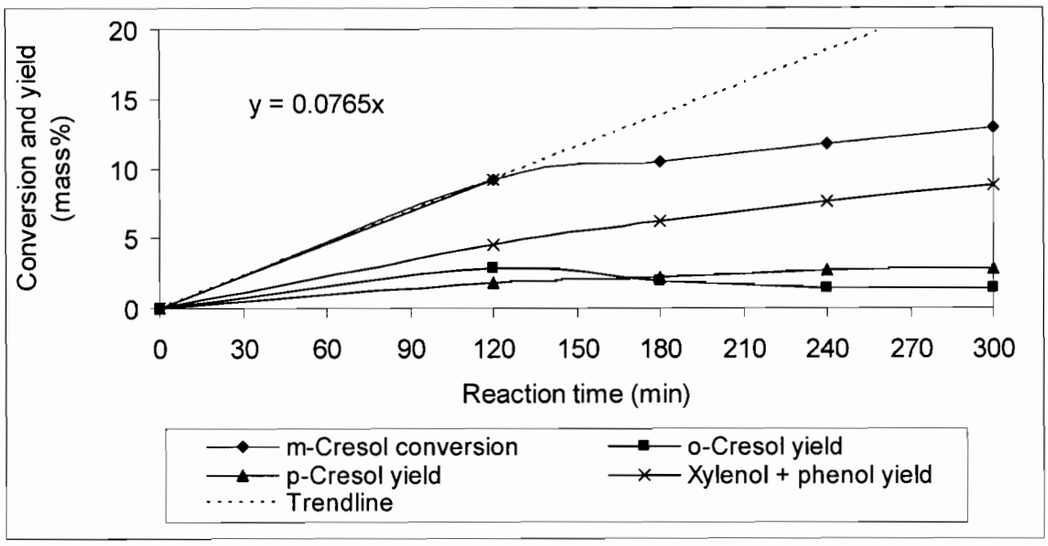


Figure 5.13: Conversion of m-cresol and yield of products, o- and p-cresol and phenol and xylenols, obtained over HBeta as a function of reaction time at temperature 250°C during the batch-wise liquid phase m-cresol isomerisation in an autoclave reactor.

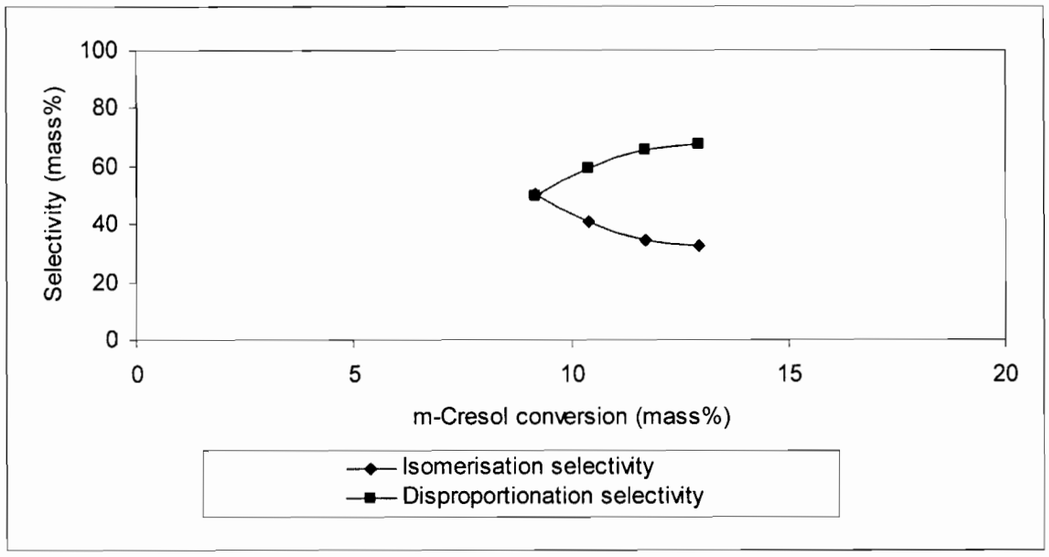


Figure 5.14: Reaction selectivity as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

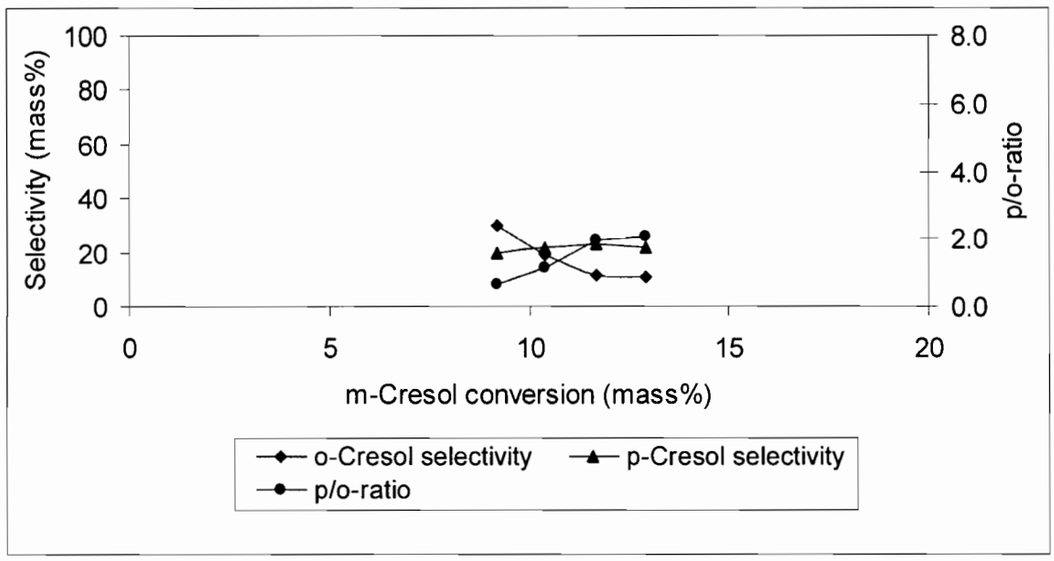


Figure 5.15: Selectivity for o- and p-cresol as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

When compared to reaction over HZSM5, the conversion and yield of major products for m-cresol isomerisation over HBeta (Figure 5.13) proved to be xylenols and phenol and a constant increase was discernable. An initial increase in o-cresol, even above p-cresol, was observed but decreased with time and it seems to level out while a slight increase in p-cresol was noticeable. The initial isomerisation and disproportionation selectivity was practically the same but an immediate increase in disproportionation with consequential decrease in isomerisation selectivity was observed (Figure 5.14) with increasing conversion. Practically constant p-cresol selectivity was observed with an initial lower level than o-cresol and decreasing o-cresol selectivity with increasing conversion was noticeable and as a result an increasing p/o-ratio (Figure 5.15) was obtained, and this differs from m-cresol transformation over HZSM5 (Figure 5.12). However, the p/o-ratio of 3.5 obtained over HZSM5 is always higher than that obtained over HBeta (0.5 - 2.0).

5.1.2.3 m-Cresol conversion over zeolite HMordenite

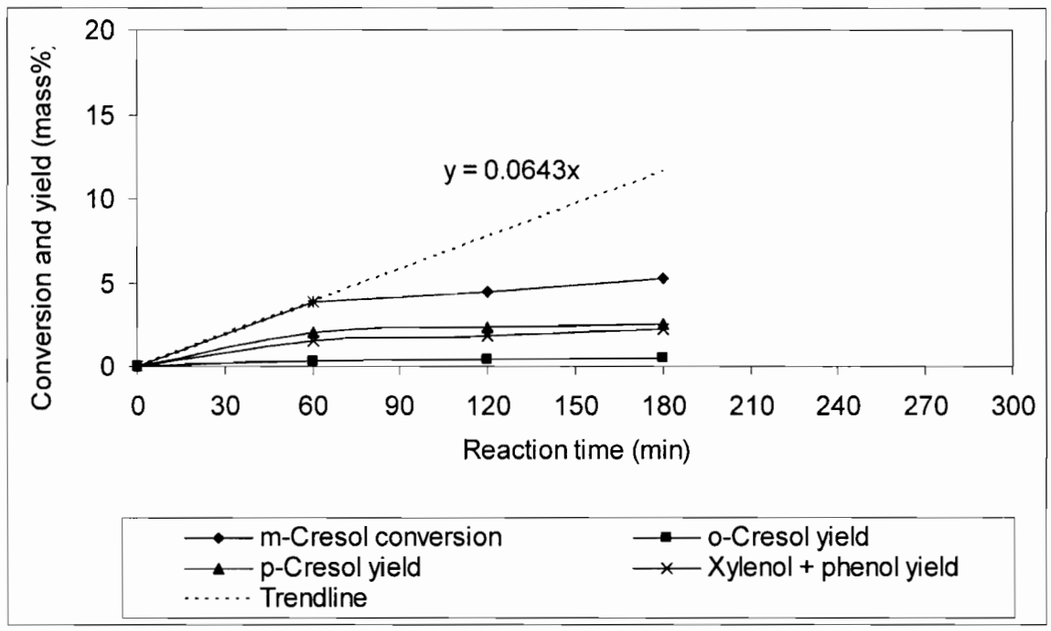


Figure 5.16: Conversion of m-cresol and yield of products, o- and p-cresol and phenol and xylenols, obtained over HMordenite as a function of reaction time at 250°C during the batch-wise liquid phase m-cresol isomerisation in an autoclave reactor.

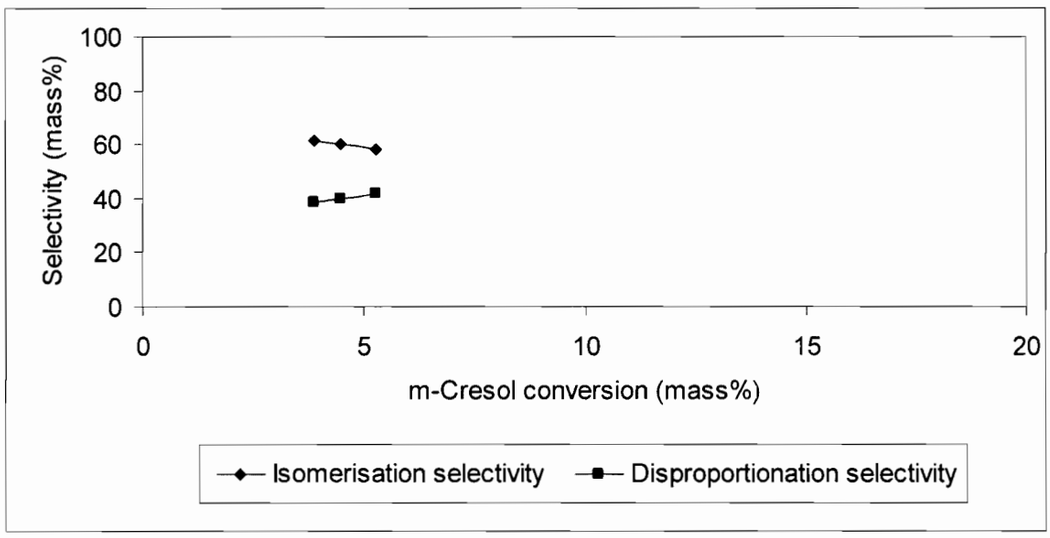


Figure 5.17: Reaction selectivity as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HMordenite at 250°C in an autoclave reactor.

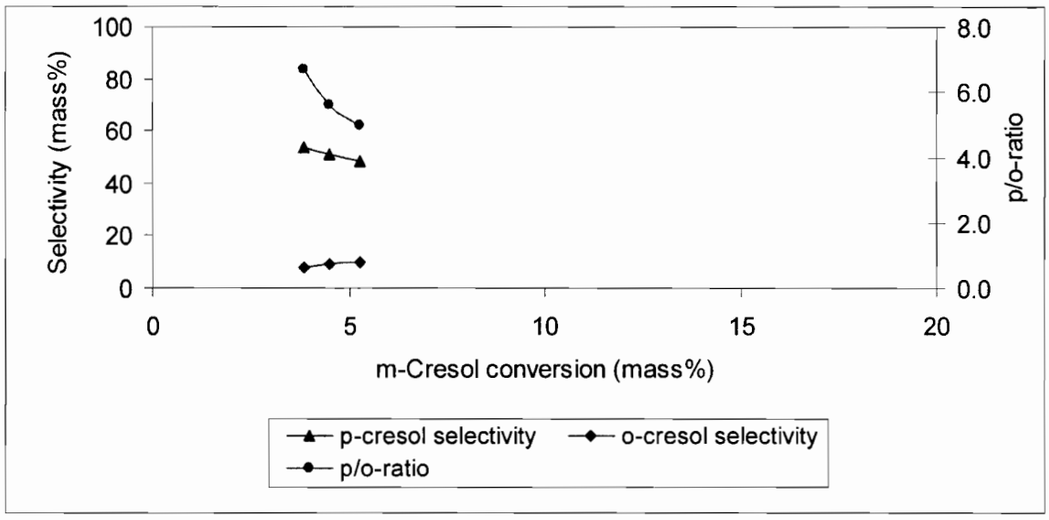


Figure 5.18: Selectivity for o- and p-cresol as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HMordenite at 250°C in an autoclave reactor.

Initially, in m-cresol transformation over HMordenite (Figure 5.16), conversion was observed but the conversion remained constant for the duration of the reaction time and as expected the major products, o-, p-cresol and xylenols and phenol, also maintained a constant yield and the perceived slight increase is not worth mentioning. Regardless of the initial higher isomerisation selectivity, a tendency towards disproportionation was observed with increasing conversion (Figure 5.17). A decrease in p-cresol selectivity and p/o-ratio with a slight increase in o-cresol selectivity was noticeable with increasing conversion (Figure 5.18). Nevertheless, is it worthwhile to note that the p/o-ratio obtained over HMordenite is still higher than that seen over the other catalysts.

5.1.3 p-Cresol conversion

p-Cresol was isomerised under the same conditions employed for o-cresol.

5.1.3.1 p-Cresol conversion over zeolite HZSM5

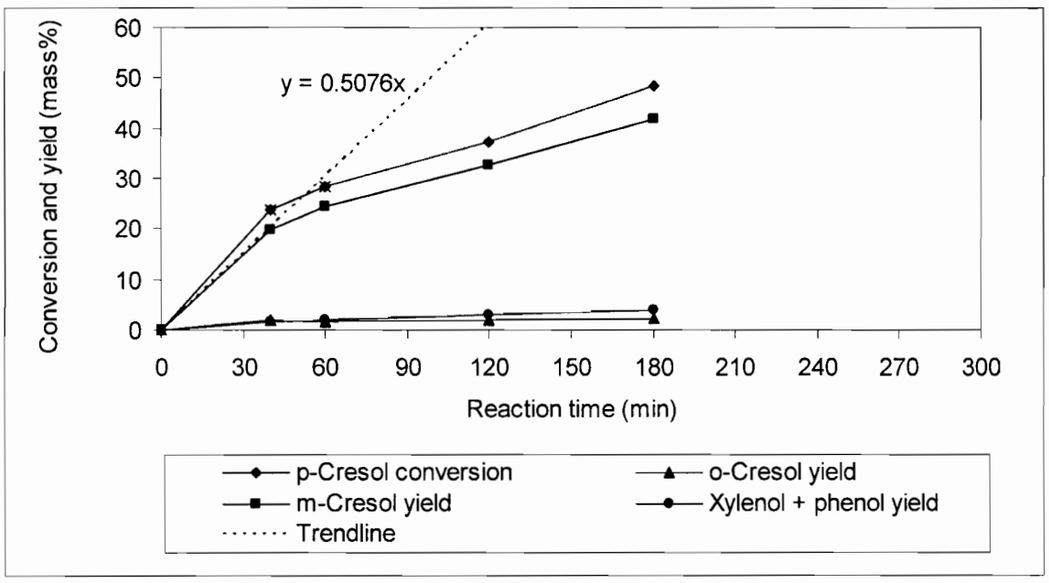


Figure 5.19: Conversion of p-cresol and yield of products, o- and m-cresol and phenol and xylenols, obtained over HZSM5 as a function of reaction time at 250°C during the batch-wise liquid phase p-cresol isomerisation in an autoclave reactor.

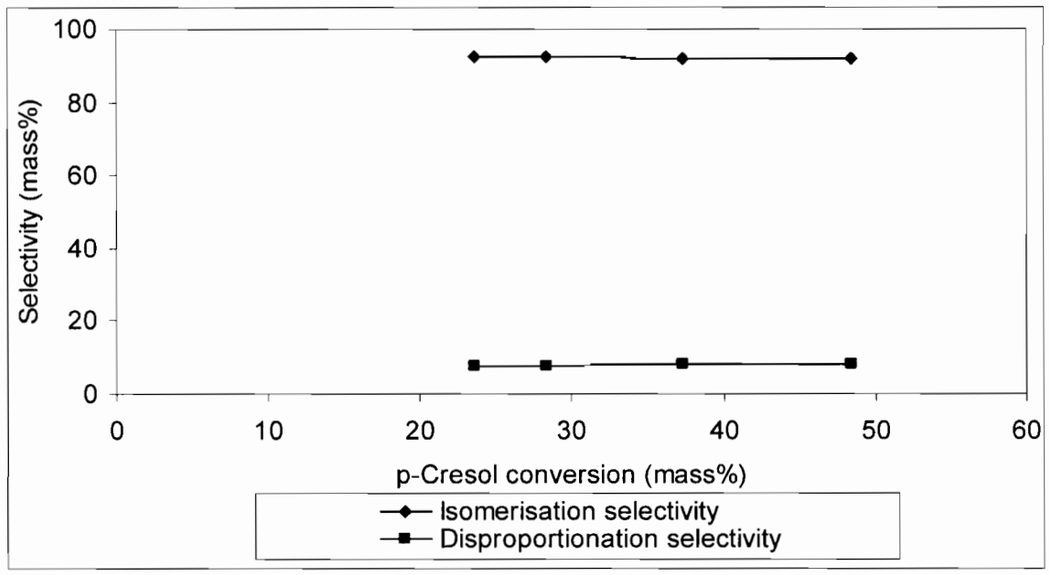


Figure 5.20: Reaction selectivity as a function of conversion during the batch-wise liquid phase p-cresol isomerisation over HZSM5 at250°C in an autoclave reactor.

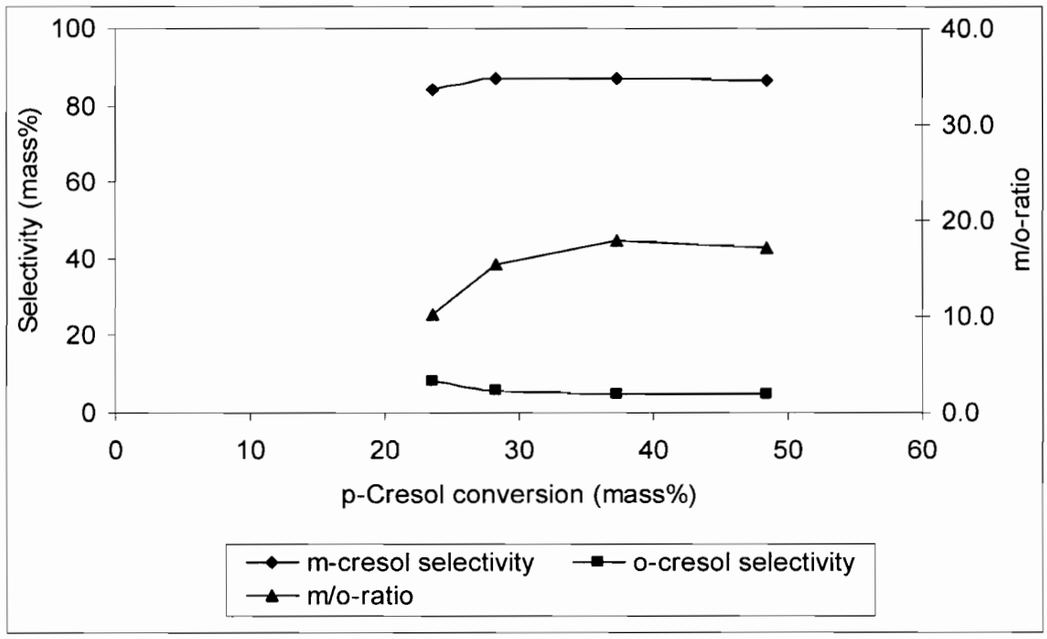


Figure 5.21: Selectivity for o- and m-cresol as a function of conversion during the batch-wise liquid phase p-cresol isomerisation over HZSM5 at 250°C in an autoclave reactor.

Figure 5.19 illustrates p-cresol conversion and yields of major products as a function of reaction time. The major product was m-cresol followed by xylenols and phenol with o-cresol in lowest yield. Despite the small difference, the yield of xylenol and phenol was slightly higher than o-cresol and both remained almost constant albeit the slight increase in xylenols and phenol content. High (> 90%) and constant isomerisation selectivity was obtained while low and constant disproportionation selectivity was observed for the duration of the reaction (Figure 5.20). Initial increase in m-cresol with resulting decrease in o-cresol selectivity was noticeable and thereafter remained constant for the respective levels, while an increase was also obtained in m/o-ratio with increasing conversion (Figure 5.21).

5.1.3.2 p-Cresol conversion over zeolite HBeta

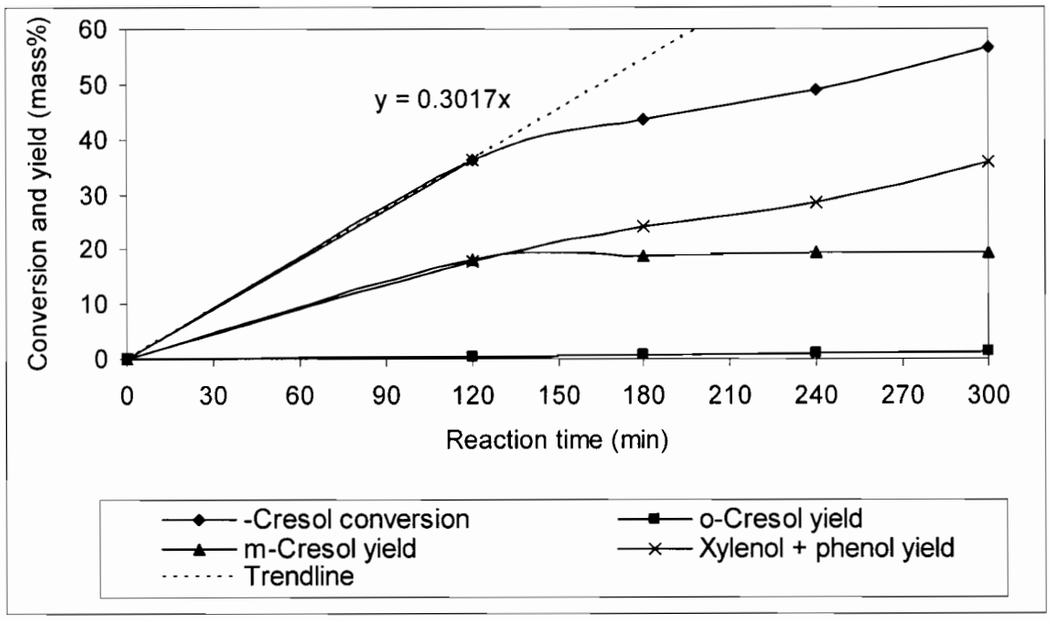


Figure 5.22: Conversion of p-cresol and yield of products, o- and m-cresol and phenol and xylenols, obtained over HBeta as a function of reaction time at 250°C during the batch-wise liquid phase p-cresol isomerisation in an autoclave reactor.

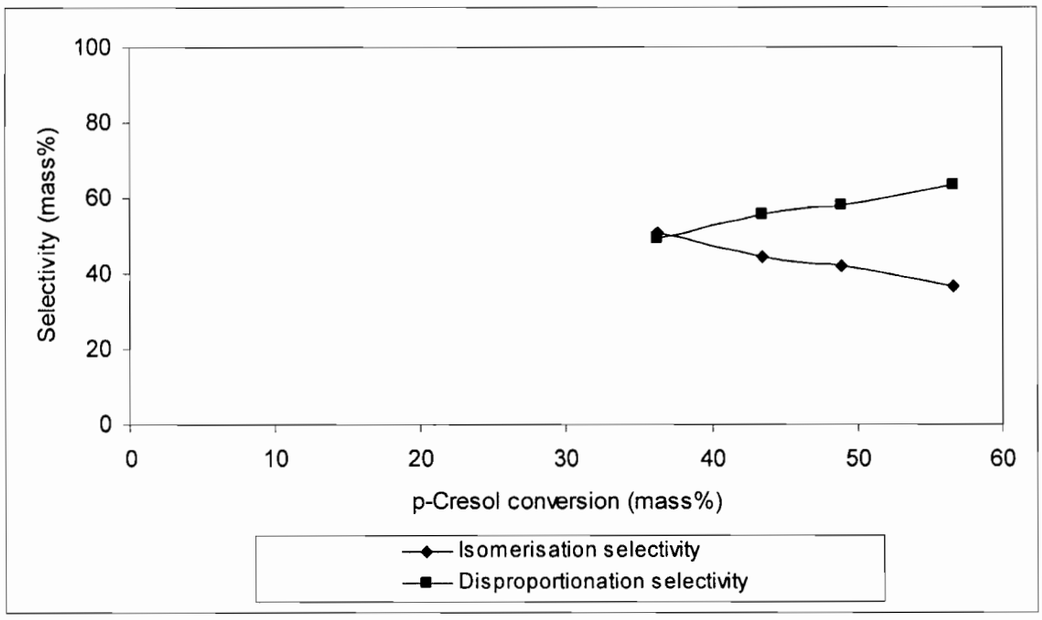


Figure 5.23: Reaction selectivity as a function of conversion during the batch-wise liquid phase p-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

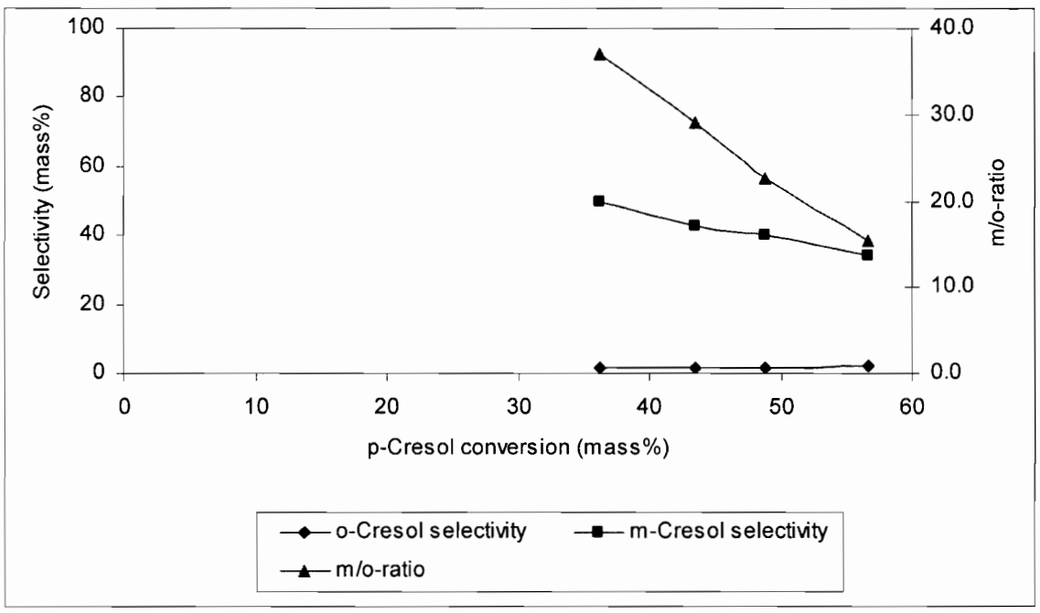


Figure 5.24: Selectivity for o- and m-cresol as a function of conversion during the batch-wise liquid phase m-cresol isomerisation over HBeta at 250°C in an autoclave reactor.

When compared to reaction over HZSM5, the conversion and yield of major products for m-cresol isomerisation over HBeta (Figure 5.22) proved to be xylenols and phenol and a constant increase was discernible. Initial increase in m-cresol (up to 120 minutes) was observed but it leveled out while a slight increase in p-cresol (very low level) was noticeable. The initial isomerisation and disproportionation selectivity was practically the same but an immediate increase in disproportionation with consequential decrease in isomerisation selectivity was observed (Figure 5.23) with increasing conversion. Practical constant o-cresol selectivity was observed with decreasing m-cresol selectivity and m/o-ratio with an increase in p-cresol conversion (Figure 5.24).

5.1.3.3 p-Cresol conversion over zeolite HMordenite

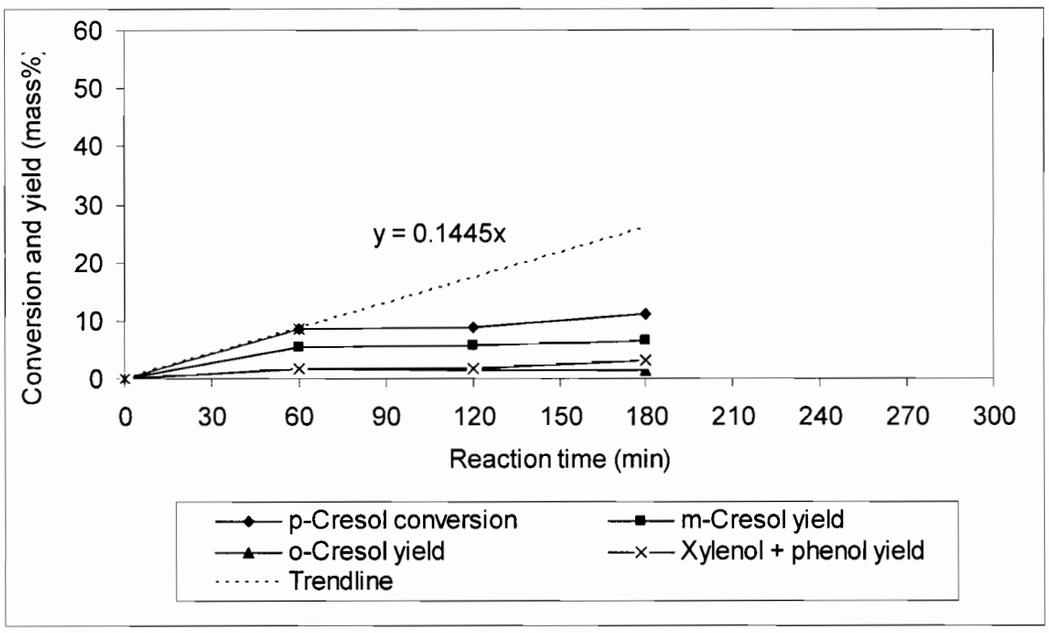


Figure 5.25: Conversion of p-cresol and yield of products, o- and m-cresol and phenol and xylenols, obtained over HMordenite as a function of reaction time at 250°C during the batch-wise liquid phase p-cresol isomerisation in an autoclave reactor.

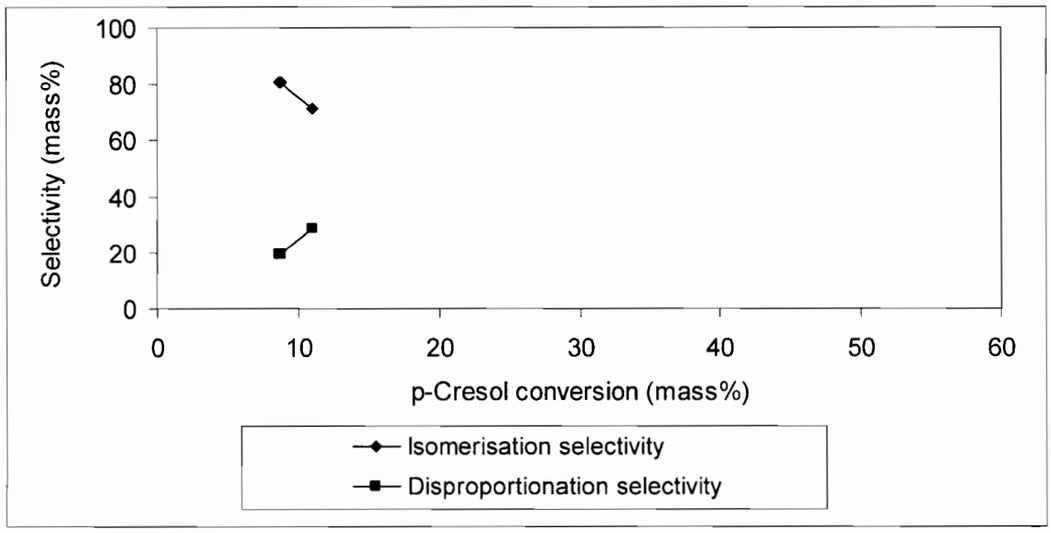


Figure 5.26: Reaction selectivity as a function of conversion during the batch-wise liquid phase p-cresol isomerisation over HMordenite at 250°C in an autoclave reactor.

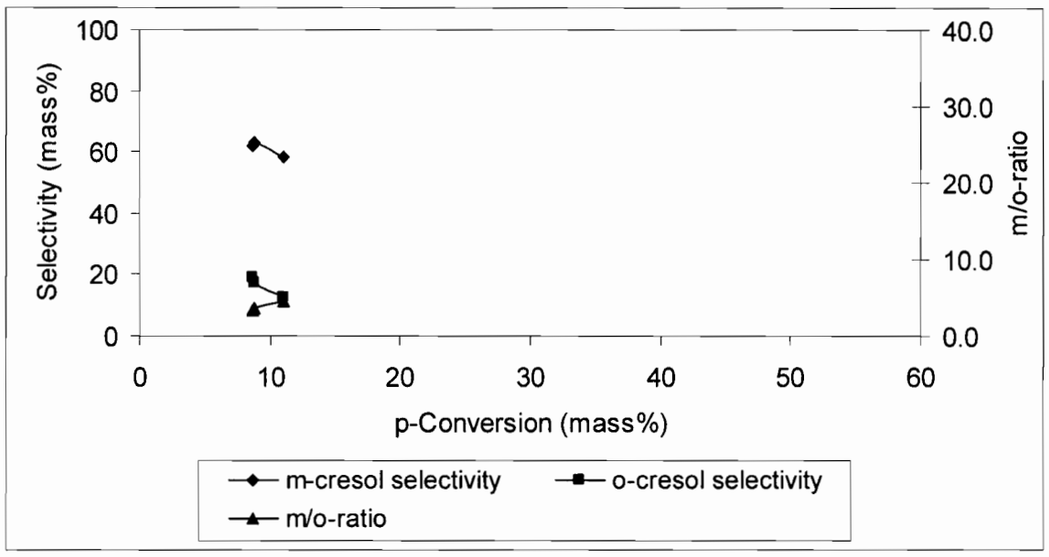


Figure 5.27: Selectivity for o- and m-cresol as a function of conversion during the batch-wise liquid phase p-cresol isomerisation over zeolite HMordenite at temperature 250°C in an autoclave reactor.

Initially, in p-cresol transformation over HMordenite, conversion increased noticeably, although on low level, as well as formation of major products, but then it remained almost unchanged (Figure 5.25). Decline in isomerisation was obtained with a tendency towards increasing disproportionation with increasing p-cresol conversion and this is depicted in Figure 5.26. A decline in o- and m-cresol selectivity was noticeable and as a result an increase in m/o-ratio was obtained (Figure 5.27).

5.2 Continuous vapour phase isomerisation

In view of the fact that catalyst deactivation occurred during the isomerisation of the three cresol isomers when performed batch-wise in the liquid phase (as a first round), the aim of this part of the investigation was to evaluate the isomerisation of o-cresol over zeolites HZSM5, HBeta and HMordenite in the vapour phase and that way, eliminate the effect of feed depletion on reaction rate and selectivity, so that catalyst deactivation as well as the effect of deactivation on conversion and selectivity could be studied independently. With that in mind, plotting selectivity data vs. conversion is intended to illustrate qualitatively selectivity changes that occurred as a result of increasing deactivation (see for instance figures 5.30 and 5.36). Moreover, the analysis of performance of continually deactivating catalyst is complicated and makes the interpretation of some of the results shown below impossible.

5.2.1 o-Cresol conversion

o-Cresol conversion over HZSM5

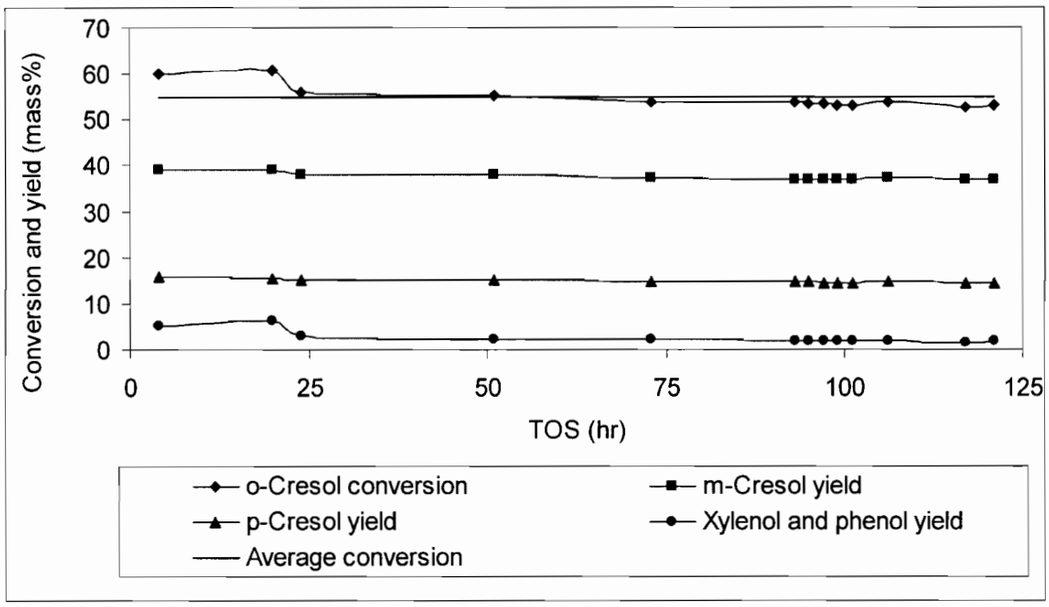


Figure 5.28: Conversion of o-cresol and yield of products, m- and p-cresol and phenol and xylenols, obtained over HZSM5 as a function of time-on-stream at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

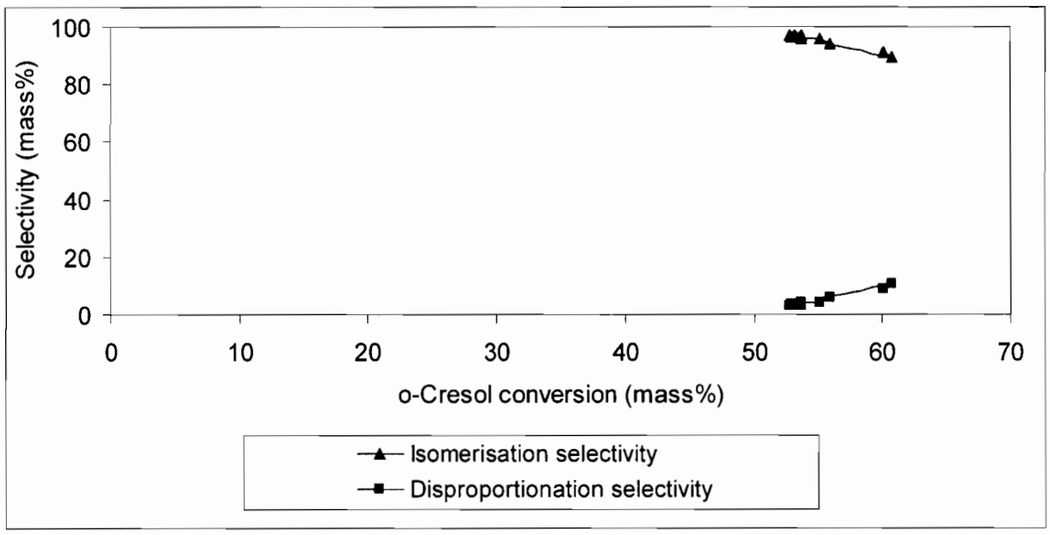


Figure 5.29: Reaction selectivity as a function of conversion over HZSM5 at temperature 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

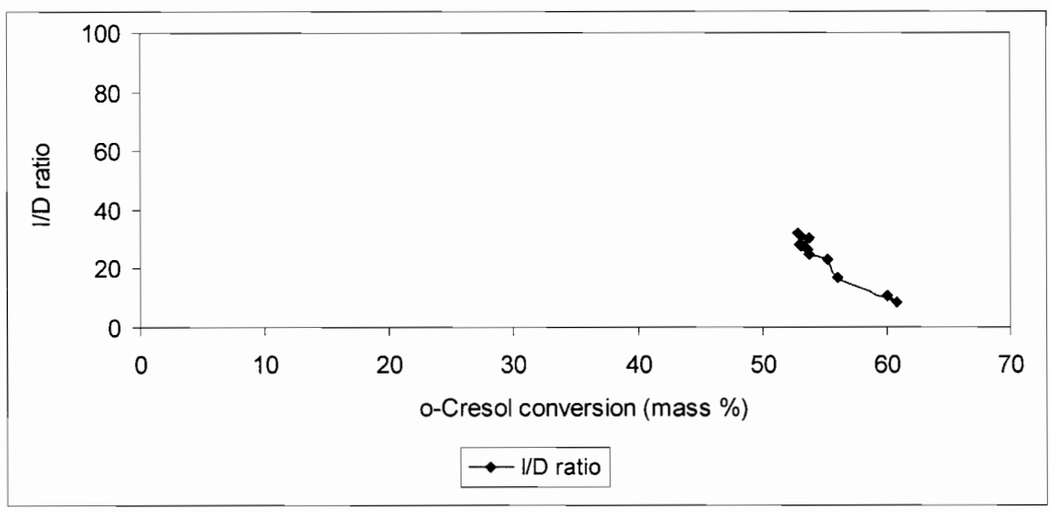


Figure 5.30: Ratio of isomerisation to disproportionation as a function of conversion over HZSM5 at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

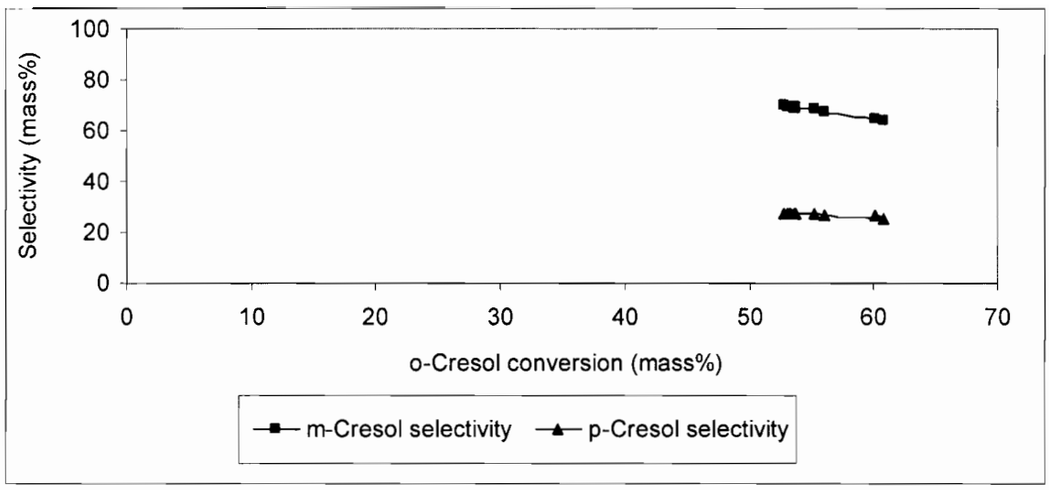


Figure 5.31: Selectivity for m- and p-cresol as a function of conversion over HZSM5 at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

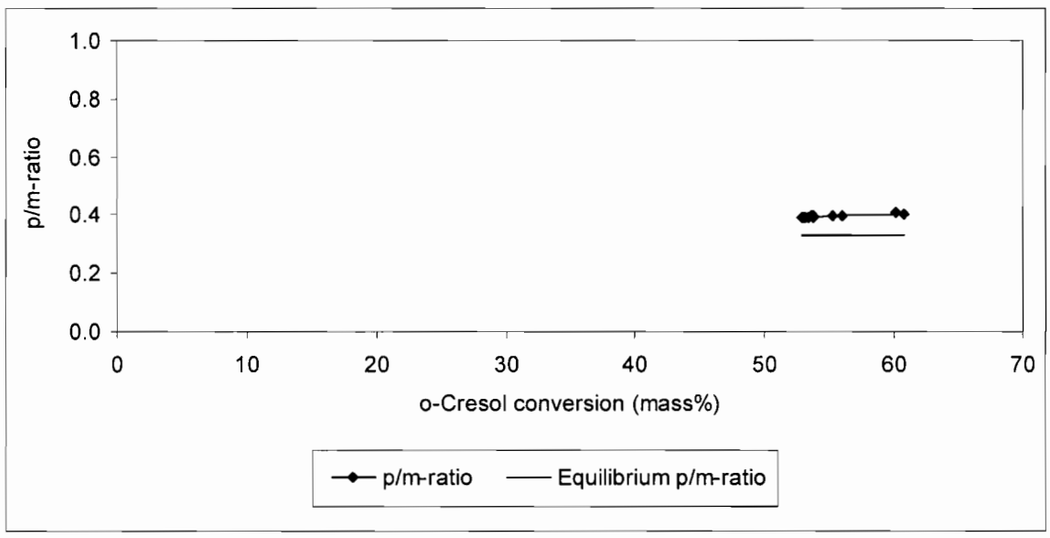


Figure 5.32: p/m-ratio as a function of conversion over HZSM5 at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

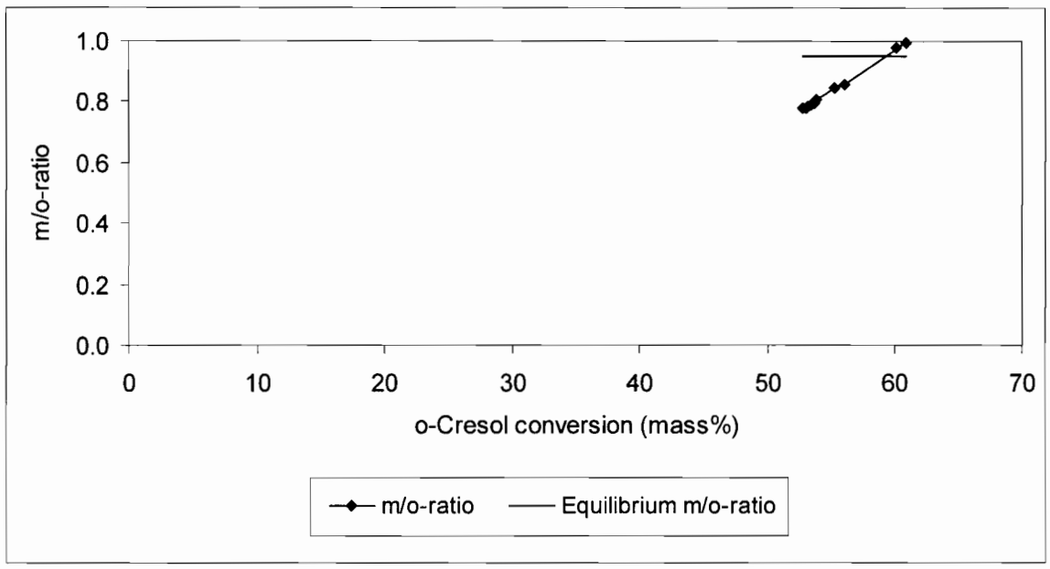


Figure 5.33: m/o-ratio as a function of conversion over HZSM5 at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

Depicted in Figure 5.28 is o-cresol conversion with the yield of major products as a function of time-on-stream over HZSM5 and the major product proved to be m-cresol followed by p-cresol and than xylenol and phenol in lowest yield. o-Cresol conversion declines very slightly with time-on-stream. The abrupt change in conversion during the initial period is considered to be due to experimental scatter. On average, o-cresol conversion was maintained at 55%, while m-cresol predominates as product (~40%) followed by p-cresol at ~15% and very low (1.7%) yields of disproportionation products phenol and xylenols. The yield of disproportionation products declined from 6.0 to 1.7% during operation (that is down to 1/3 of the initial level) in particularly during the initial period. The isomerisation selectivity was very high (>90%) while a corresponding low disproportionation selectivity (<10%) was obtained (Figure 5.29) and it was evident that at lower conversion an increase in selectivity with a corresponding decrease in disproportionation was noticeable (I/D ratio, Figure 5.30). It was also discernable (Figure 5.31) that the selectivity towards m- and p-cresol increased with a decrease in conversion, but the selectivity for m-cresol (~70%) remained

higher than for p-cresol (~30%). A p/m-ratio of 0.4 (Figure 5.32) was obtained, which is above the equilibrium p/m distribution (0.33) as reported by Imbert[41], while the m/o-ratio approached equilibrium values as illustrated in Figure 5.33.

5.2.1.2 o-Cresol conversion over HBeta

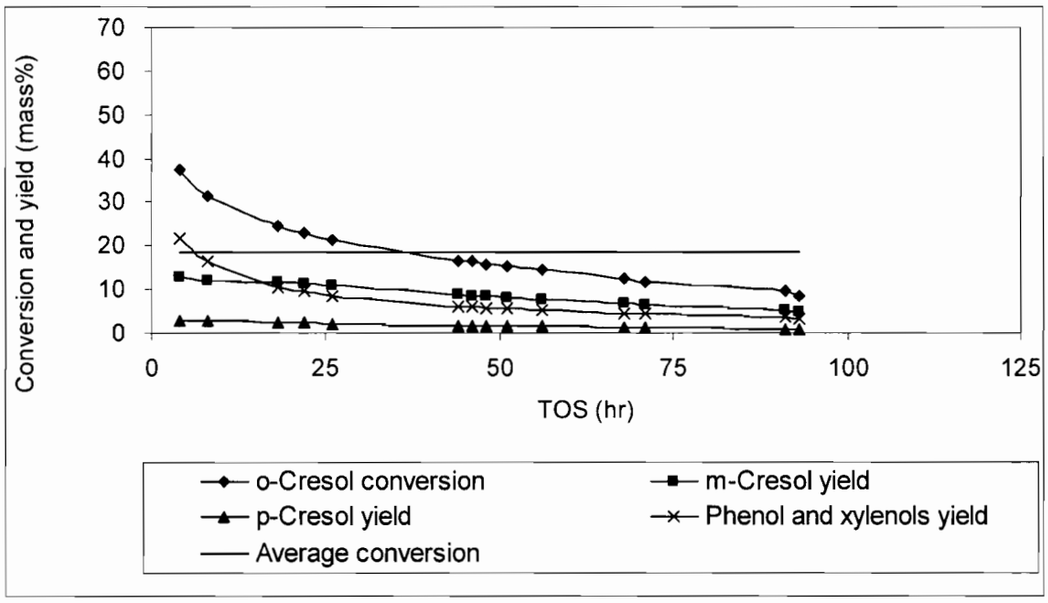


Figure 5.34: Conversion of o-cresol and yield products, m- and p-cresol and phenol and xylenols, over HBeta as a function of time-on-stream at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

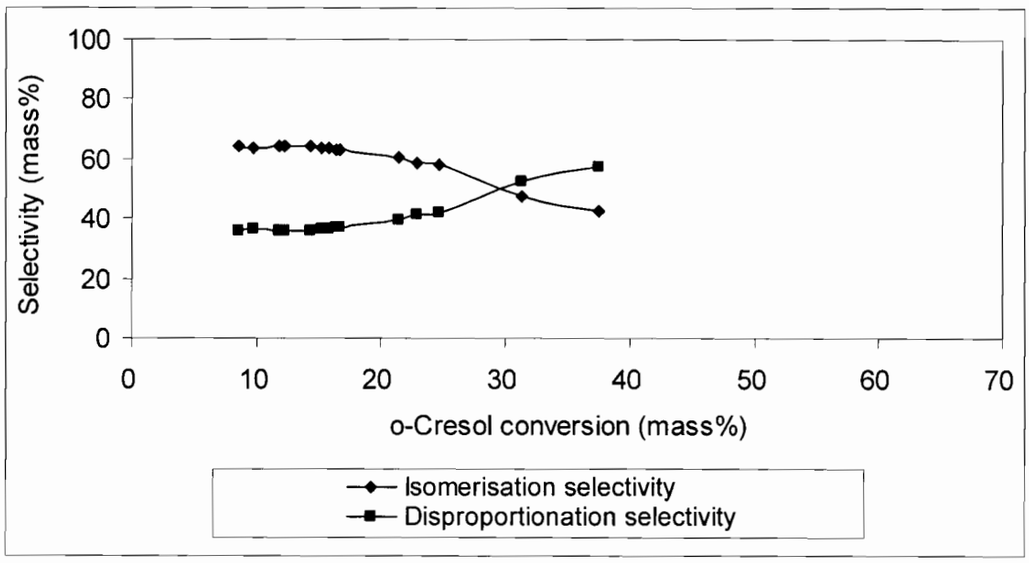


Figure 5.35: Reaction selectivity as a function of conversion over HBeta at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

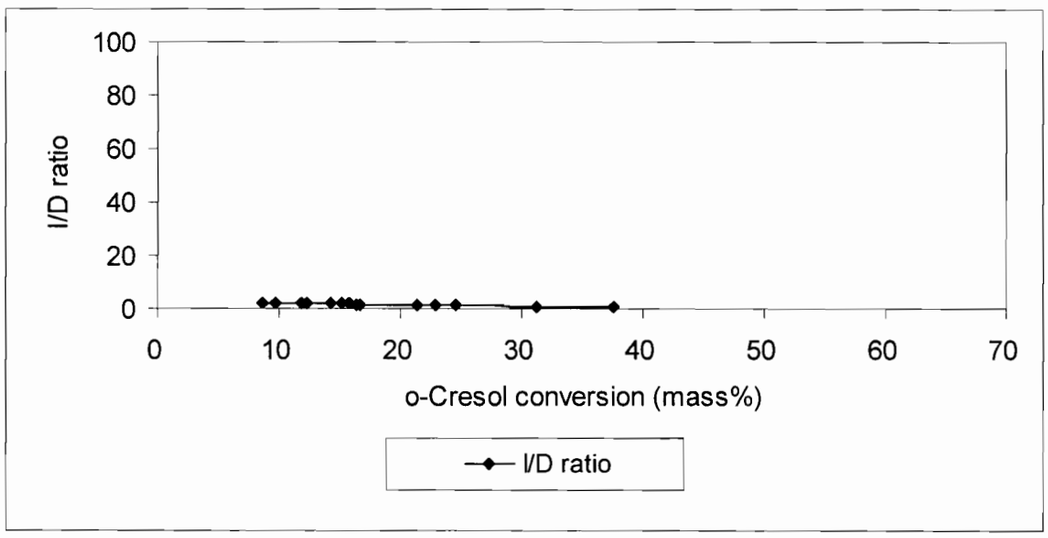


Figure 5.36: Ratio of isomerisation to disproportionation as a function of conversion over HBeta at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

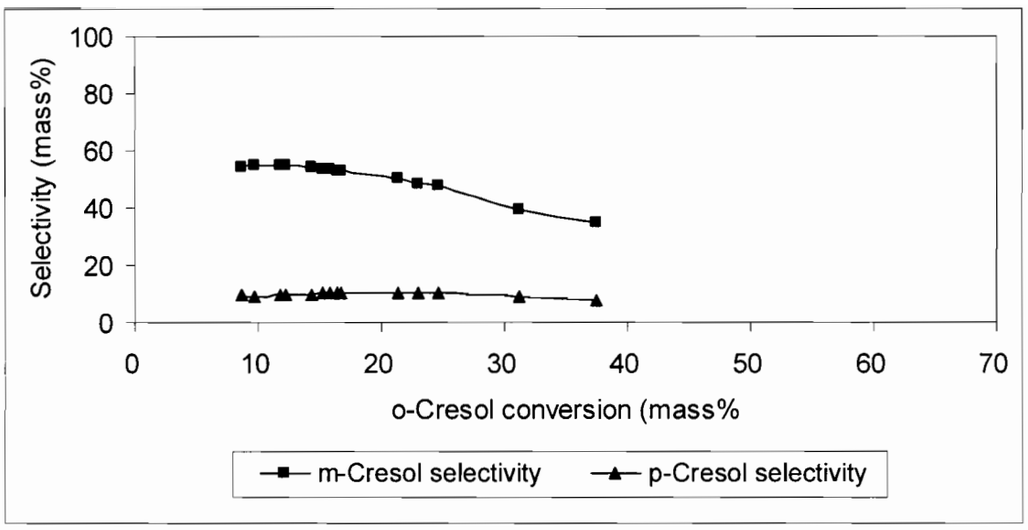


Figure 5.37: Selectivity for m- and p-cresol as a function of conversion over HBeta at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

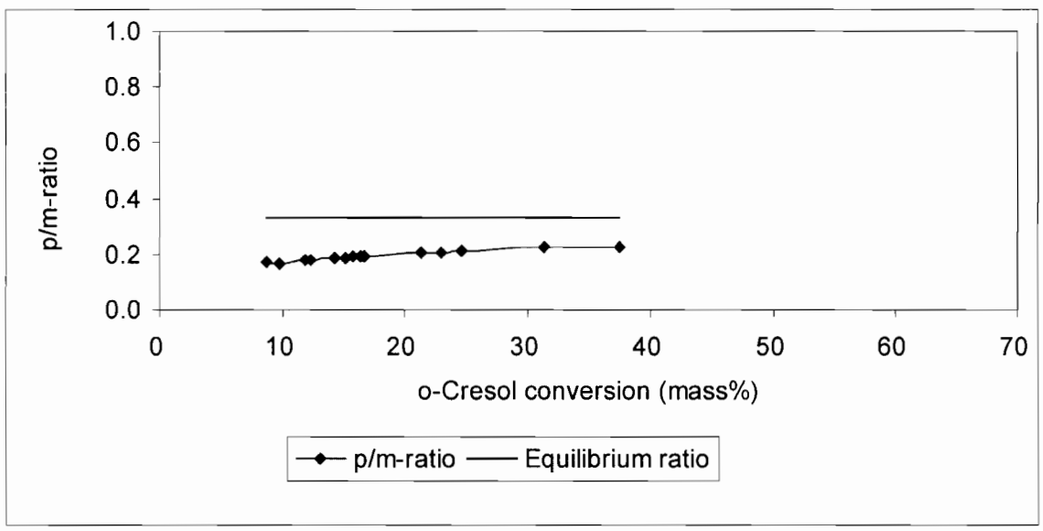


Figure 5.38: p/m-ratio as a function of conversion over HBeta at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

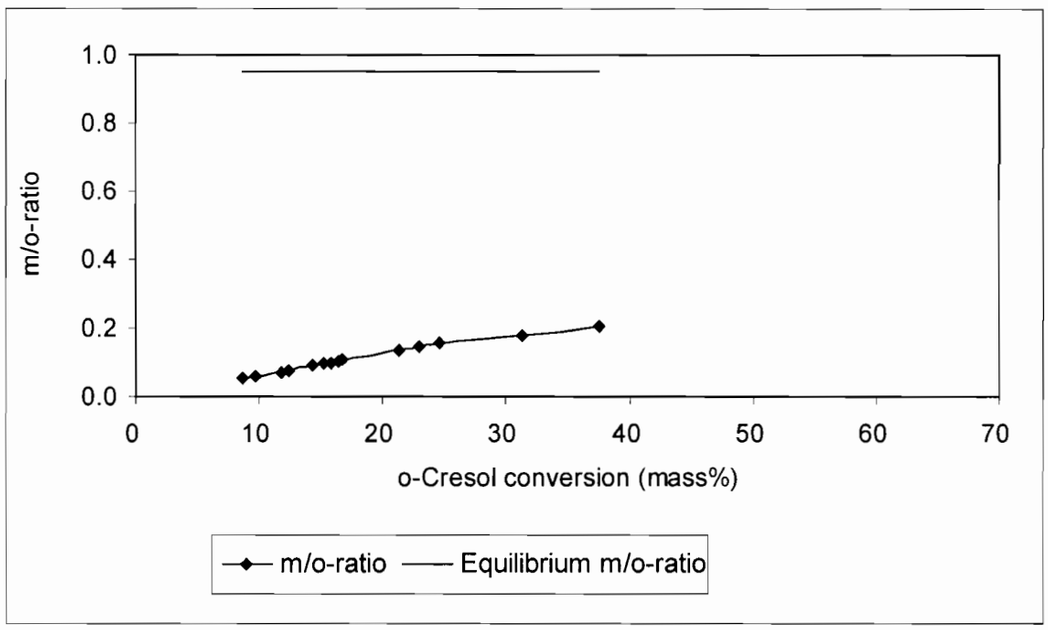


Figure 5.39: m/o-ratio as a function of conversion over HBeta at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

A gradual decline in o-cresol conversion (37.5 to 8.6%) was discernible over HBeta (Figure 5.34) with increasing time-on-stream and initially (first 8 hours) the disproportionation products were higher than the isomerised products but decreased to between m-cresol and p-cresol formation. A decline in m- and p-cresol yield was also noted at low o-cresol conversion. Higher isomerisation selectivity was observed (at low conversion) but with increasing conversion (>30%) disproportionation selectivity (Figure 5.35) is preferred and this is also illustrated in the I/D-ratio (Figure 5.36). m-Cresol formation predominates and a slight decline with increasing conversion was observed (Figure 5.37), while selectivity towards p-cresol remained constant at < 10%.

The p/m-ratio obtained (0.2) during this investigation was below the equilibrium p/m-ratio (Figure 5.38) and an increase is visible with increasing o-cresol conversion. At the same time the m/o-ratio (Figure 5.39) was also way below the equilibrium with the same trend as p/m.

5.2.1.3 o-Cresol conversion over zeolite HMordenite

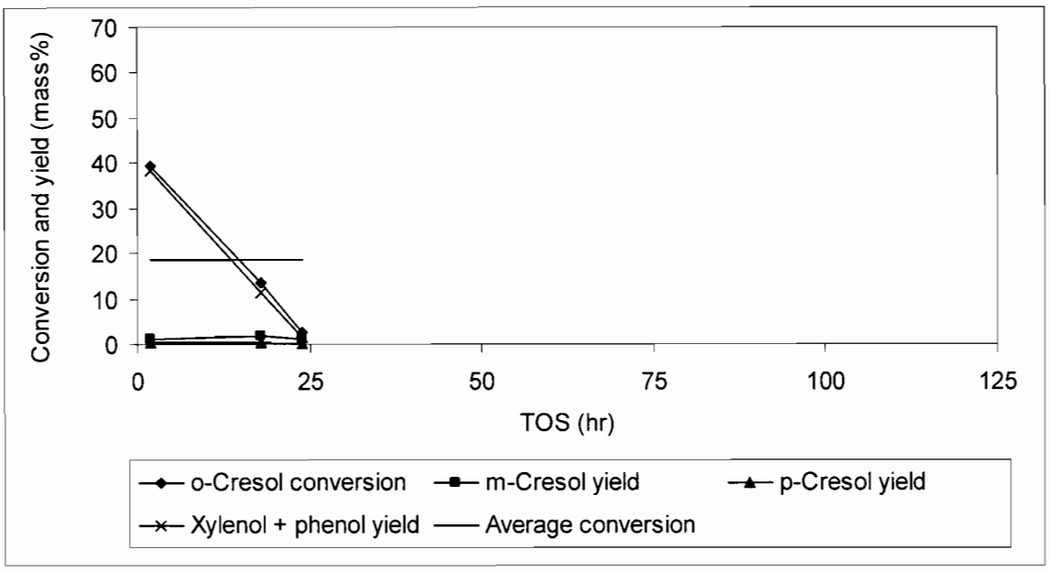


Figure 5.40: Conversion of o-cresol and yield of products, m- and p-cresol and phenol and xylenols, obtained over HMordenite as a function of time-on-stream at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

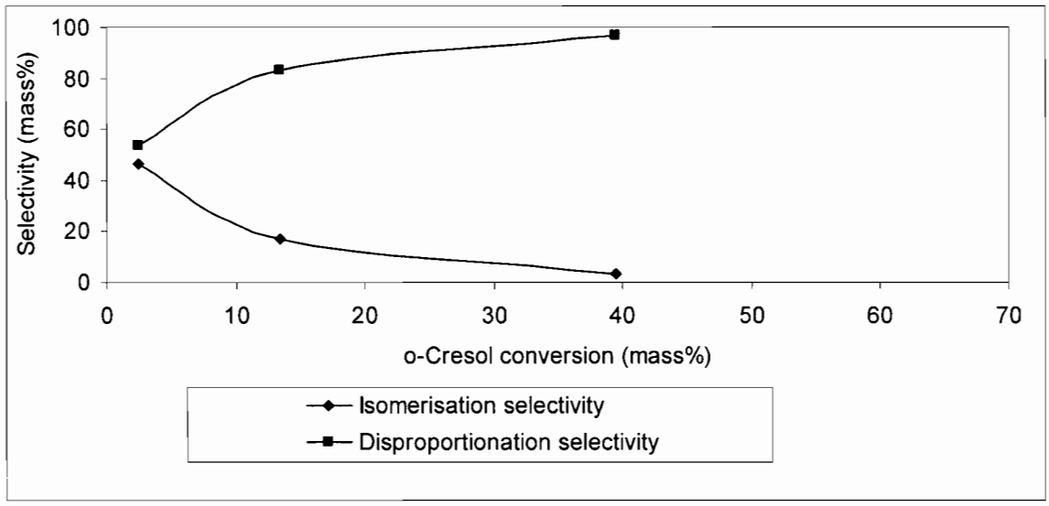


Figure 5.41: Reaction selectivity as a function of conversion over HMordenite at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

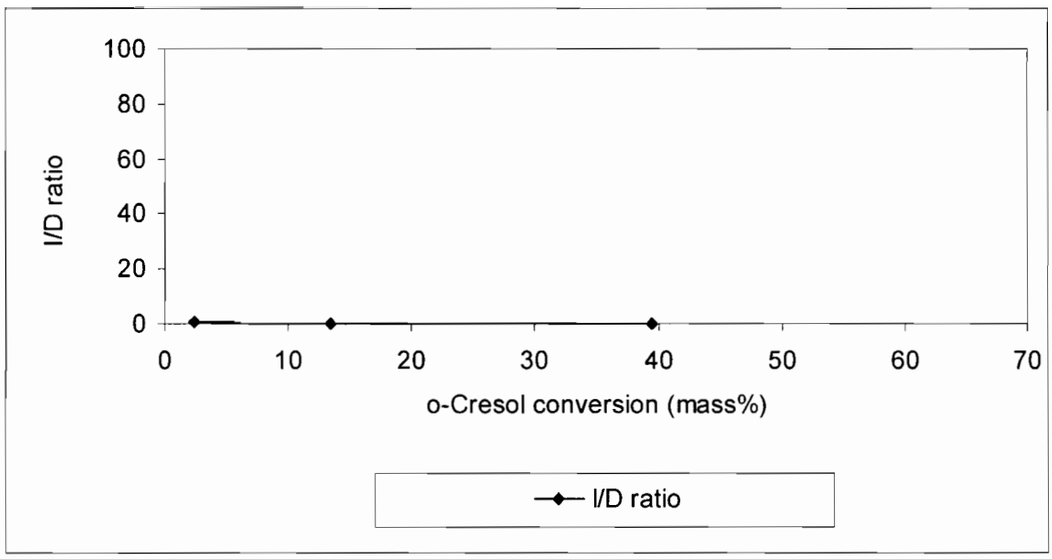


Figure 5.42: Ratio of isomerisation to disproportionation as a function of conversion over HMordenite at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

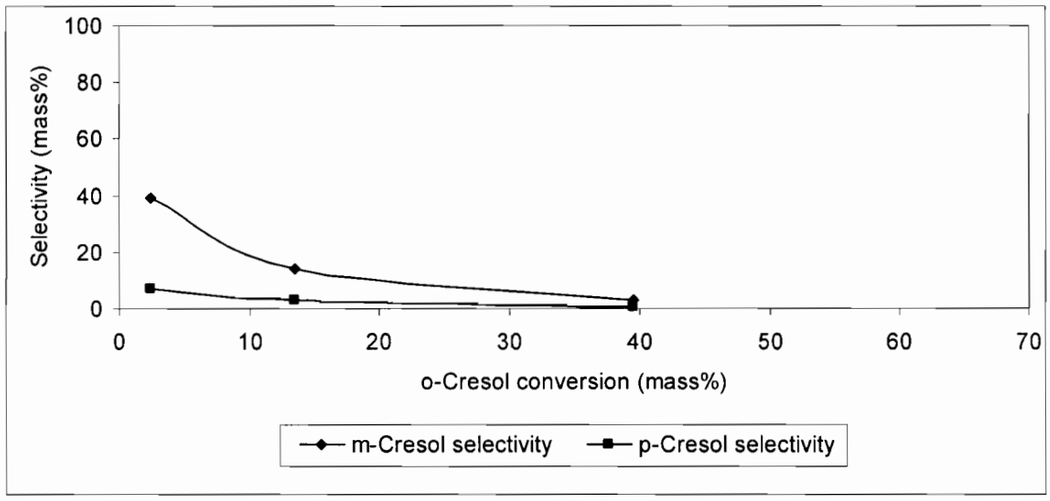


Figure 5.43: Selectivity for m- and p-cresol as a function of conversion over HMordenite at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ during the continuous vapour phase o-cresol isomerisation in a fixed-bed flow through reactor.

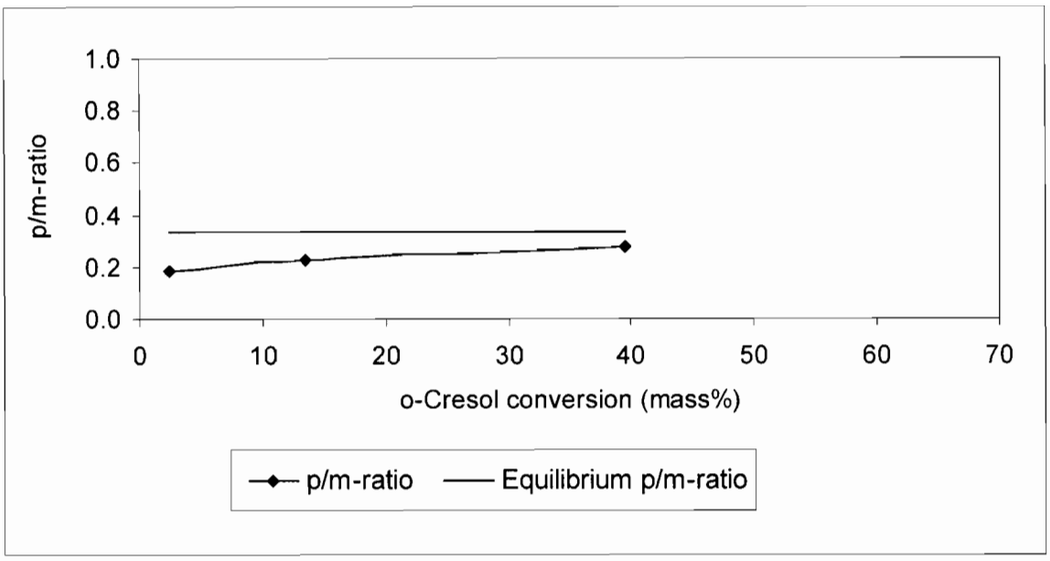


Figure 5.44: p/m-ratio as a function of conversion over HMordenite at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ in a fixed-bed flow through reactor.

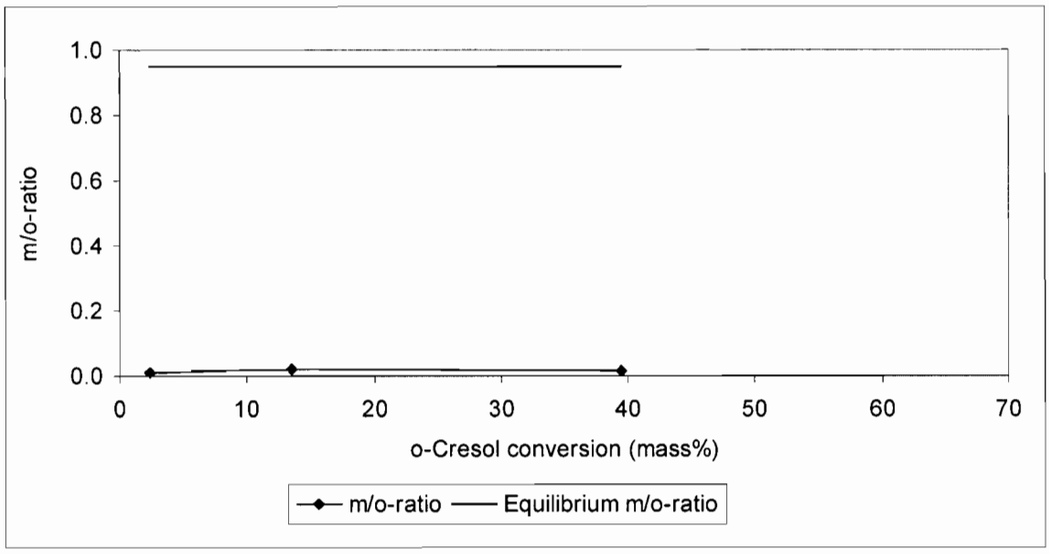


Figure 5.45: m/o-ratio as a function of conversion over HMordenite at 350°C, atmospheric pressure and LHSV of $1hr^{-1}$ in a fixed-bed flow through reactor.

A rapid decline in o-cresol conversion (39.5 to 2.4% within 24 hours) was noticeable for the transformation over HMordenite and after one day on stream no activity remained (Figure 5.40). Initially high disproportionation products (38.1%), which declined rapidly to 1.3%, were found, while very low isomerised products (<1%) were observed. A decline in conversion gave an increase in isomerisation selectivity with a resulting decrease in disproportionation (Figure 5.41). The I/D-ratio also showed a decrease with increasing o-cresol conversion (Figure 5.42). A rapid decline in m-cresol selectivity (from 40 to <2%) was noticeable and very low p-cresol selectivity (<5%) was obtained (Figure 5.43). The p/m-ratio approaches equilibrium (at high conversion) but is still below the equilibrium ratio even after the catalyst was deactivated (Figure 5.44) and a resulting low m/o-ratio was also noted (Figure 5.45).

6. DISCUSSION

6.1 Batch-wise liquid phase isomerisation

As a first round investigation into the isomerisation of o-, m- and p-cresol, the reaction of these compounds over zeolites HZSM5, HBeta and HMordenite were studied in batch mode. Since isomerisation is almost always accompanied by disproportionation/transalkylation, special attention towards this aspect of the reaction was given throughout the study.

6.1.1 o-Cresol conversion over zeolite HZSM5, HBeta and HMordenite

6.1.1.1 Conversion[1] and activity

An o-cresol conversion of 9.9, 16.3 and 8.9% respectively was obtained over HZSM5 (Figure 5.1), HBeta (Figure 5.4) and HMordenite (Figure 5.7) after reaction time of 180 minutes. The better conversion of HBeta, when compared to the other zeolites, is probably explicable in terms of pore size, where the pore size of HBeta is 6.4 x 7.6 Å compared to that of HZSM5 (5.1 x 5.5 Å) and HMordenite (6.7 x 7.0 Å). Note that the pressure drop during operation was only about 2 bar (refer to the revised section 4.1.4 and revised table 4.1). In addition, it can be expected that the pressure has no effect on the liquid phase reaction since there is no light co-reactant or co-product and since the major products boil very close to the feed.

Despite the poor conversion over HZSM5 (equilibrium conversion of o-cresol in isomerisation reaction is 64% as reported by Imbert et al.41), an interesting product distribution was observed over time. As the reaction progressed, phenol and xylenol levels remained constant (1.15%) while an increase was observed for m-cresol (up to 7.4%) and p-cresol (up to 1.1%). After one hour, cited literature values of 23.0, 35.8 and 12.3% for phenol and xylenol, m- and p-cresol

[1] Catalyst comparison is generally done at similar or the same conversion, preferably at low conversion.

respectively were reported, which was much higher than what was seen during the current study (1.1, 2.6 and 0.2%). Over HBeta, an increasing xylenol and phenol yield (6.0-11.4%) was found with m-cresol slightly increasing (2.6-4.7%) and p-cresol remaining constant and low (0.7%). In this instance, the yield of the byproducts (11.4%) remained much higher than m- and p-cresol. Constant but slightly higher xylenol and phenol products (4.2%) were also yielded over HMordenite with a slight increase in p-cresol (1.3-1.9%) and constant m-cresol (2.8%). HZSM5 has a greater capacity to impose shape-selectivity than HBeta and HMordenite and this probably led to the difference in product distribution observed for this catalyst.

The activity[2] (Table 6.1) of the different catalysts was estimated by the slopes of the first 60 minutes of reaction time except for HBeta, where 120 minutes was used (Figure 5.1, 5.4 and 5.7). Although HMordenite proved to have the highest activity over the first 60 minutes of reaction, is it evident that this catalyst is rapidly deactivated after the initial period (<1% increase in conversion after 120 minutes).

Table 6.1 Activity data deduced from the slopes after 60 minutes of o-cresol conversion in the liquid phase.

	Activity
Catalyst	gcresol/gcat/min
HZSM5	0.151
HBeta*	0.169
HMordenite	0.291

* Data deduced at 120 minutes because no sample was taken at 60 minutes

[2] During this study, activity is define as relative activity to give some semi-quantitative interpretation of the differences between catalyst samples and the data obtained is not suitable for a serious kinetic (i.e. activity) analysis.

6.1.1.2 Selectivity

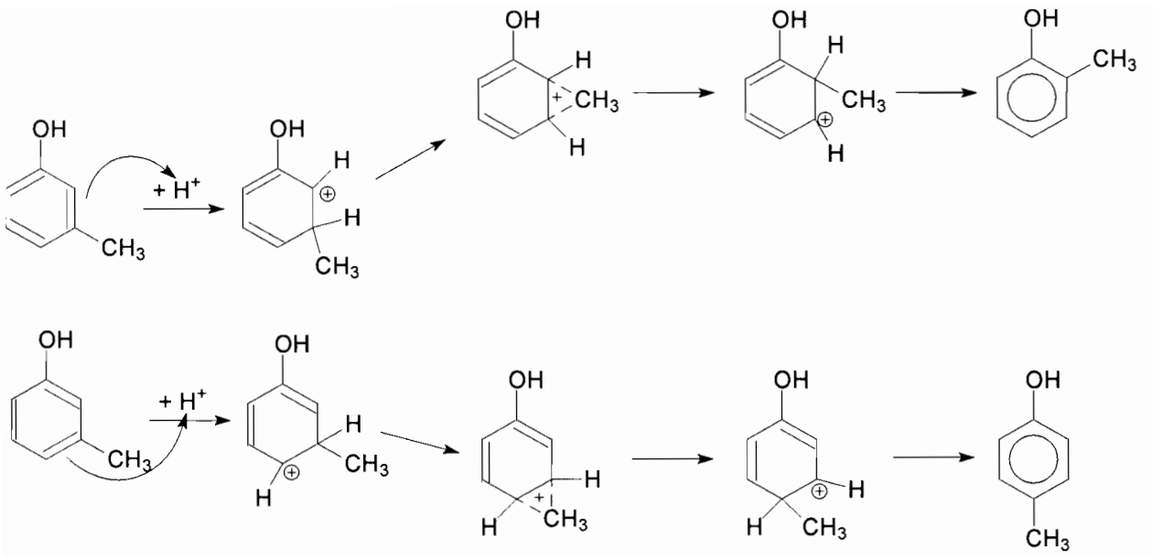
6.1.1.2.1 Isomerisation vs. disproportionation

- Definition of isomerisation and disproportionation

The acid catalysed movement of methyl groups around an aromatic ring (cresols, xylenes, etc.) can be envisaged to happen in one of two ways: after protonation of the aromatic ring, a 1,2-methyl shift can lead to a different isomer (isomerisation) or methyl group(s) can be transferred between different aromatic rings (disproportionation)

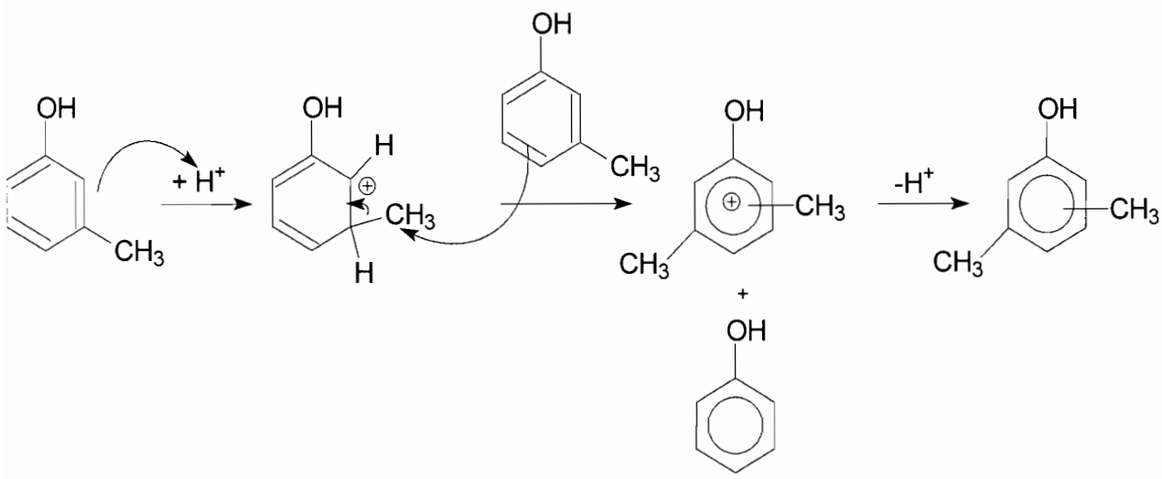
- Mechanism

The unimolecular isomerisation mechanism involves transformation of one benzenium ion intermediate to another through a methyl shift (Scheme 6.1). This occur mainly when the pores of the zeolite is of such a nature that only one substrate molecule can fit into the pore, in other words a methyl group cannot be transferred to another aromatic ring. When the pore size of the zeolite allows bimolecular reaction, disproportionation by intermolecular methyl transfer (scheme 6.2) occurs as well.



Scheme 6.1 Proposed mechanism for m-cresol isomerisation over zeolites

With large pore zeolites a secondary disproportionation or transalkylation process occurs. After protonation of the ring, a methyl group is transferred to the neighbouring aromatic ring and phenol and xylenols are formed (Scheme 6.2). When a successive (consecutive) reaction occurs between m-cresol and xylenol, o-cresol and trimethyl phenols are yielded. Through this bimolecular pathway, there is a preferential formation of o-cresol from m-cresol isomerisation.



Scheme 6.2 Proposed bimolecular pathway for m-cresol disproportionation over zeolites

- *Discussion*

The isomerisation selectivity for the three zeolites tested (HZSM5, HBeta and HMordenite) was found to be 86.3, 36.0 and 56.3% while disproportionation accounted for 13.7, 64.0, and 43.7% for HZSM5 (Figure 5.2), HBeta (Figure 5.5) and HMordenite (Figure 5.8) respectively. The preference for isomerisation over HZSM5 can be attributed to the shape-selectivity and the pore size of this catalyst, while the disproportionation observed can probably be attributed to the initial activity on the external surface of the zeolite. Having larger pore sizes, higher disproportionation selectivity may be expected over HBeta and HMordenite. It can be assumed that bulky by-products (i.e. the higher co-products from the disproportionation reaction) can form inside the wide pore zeolites (HBeta and HMordenite). Since intra-crystalline mass transfer can be expected to be greater in HBeta with its three dimensional interconnected pore system, higher disproportionation selectivity than over HMordenite, as observed, can be expected. Over the medium pore zeolite HZSM5, it can be assumed that transalkylation reactions occur mainly on the external surface, hence the low transalkylation selectivity and high isomerisation selectivity (on average 86%) that was observed. It can also be assumed that bulky oligomers (i.e. "soft coke") that have formed at the comparably low reaction temperature of 250°C block access to pores inside the crystals of HBeta and HMordenite (not so much inside medium pore HZSM5). HBeta and HMordenite have larger pore sizes than HZSM5 and therefore are more prone to allow the formation inside the pores of the larger oligomers. This is less likely to occur over HZSM5 with its narrower pores. HMordenite, which has a mono dimensional pore system, is very susceptible to rapid deactivation due to "coke" formation in its pores. In the case of HMordenite, it appears that the slimmest molecule (p-cresol) was the only one that could still desorb from coked HMordenite hence the increasing p-cresol and isomerisation selectivity as well as increasing p/m-ratio at higher conversion. HBeta and HZSM5 appear quite stable. The decline in disproportionation selectivity with increasing reaction time and conversion over HZSM5 may be due to selective deactivation of the external surface of the zeolite crystals. Over

HBeta, disproportionation reaction may preferentially take place inside the pore system, which is three dimensionally interconnected, hence moderate formation of "soft coke" has no immediate effect.

6.1.1.2.2 Individual selectivity and p/m-ratio

A m-cresol selectivity of 74.8, 28.1 and 34.2% respectively was obtained for reactions over HZSM5 (Figure 5.3), HBeta (Figure 5.6) and HMordenite (Figure 5.9), while selectivity towards p-cresol proved to be 11.5, 3.8 and 21.9% respectively for the three catalysts. The higher m-cresol selectivity observed for all three zeolites reflects kinetic control rather than thermodynamic control.

The p/m-ratio of 0.15 obtained over HZSM5 was, however, below the equilibrium ratio of 0.33, as reported by Imbert[41].

It can thus be concluded that isomerisation is preferred over HZSM5, while disproportionation is preferred over HBeta. Due to the rapid deactivation observed with HMordenite, it must be concluded that this catalyst is suitable for neither isomerisation nor disproportionation.

6.1.2 m-Cresol conversion over zeolite HZSM5, HBeta and HMordenite

In order to obtain a full understanding of the effect of the three zeolites on the isomerisation reaction, m-cresol was next subjected to the reaction under the same conditions as described for o-cresol.

6.1.2.1 Conversion and activity

m-Cresol conversion over HZSM5 (16.3%), HBeta (12.9%) and HMordenite (5.3%) are illustrated in Figures 5.10, 5.13 and 5.16 respectively. The higher m-cresol conversion obtained over HZSM5, when compared to the other two zeolites, is probably due to the pore size and shape-selectivity of this catalyst and is explained by the unimolecular mechanism portrayed in Scheme 6.1. The percentage m-cresol in the cresol equilibrium is 42% as reported by Imbert[40] and as a result the limit conversion is thus 58%. Since there are other products such

as phenol and xylenols that can also form, the limit conversion is even higher. The conversion over HZSM5 (Figure 5.10) and HBeta (Figure 5.13) is below the reported equilibrium and it can therefore be concluded that thermodynamics does not play a role but the reaction is controlled by mass transfer and/or kinetics. After the initial increase in conversion, HMordenite showed rapid deactivation (Figure 5.16) with no further product formation detectable. If m-cresol conversion is compared to o-cresol transformation over the three zeolites, it is only HZSM5 that gave better conversion results (16.3 vs. 9.9% for m- and o-cresol conversion respectively).

The reason for the higher activity of m-cresol over HZSM5, above the other two zeolites (Table 6.2), is plausible in terms of the 1,2-methyl shift, which is typical for zeolite HZSM5.

Table 6.2 Activity data deduced from the slopes after 60 minutes of m-cresol conversion in the liquid phase.

	Activity
Catalyst	gcresol/gcat/min
HZSM5	0.365
HBeta*	0.166
HMordenite	0.140

* Data deduced at 120 minutes because no sample was taken at 60 minutes

6.1.2.2 Selectivity

6.1.2.2.1 Isomerisation vs. disproportionation

The isomerisation selectivity was found to be 93.3, 32.3 and 58.3 for HZSM5 (Figure 5.11), HBeta (Figure 5.14) and HMordenite (Figure 5.17) respectively while disproportionation accounted for 6.7, 67.7 and 41.7%. The preference for isomerisation over HZSM5 can be explained in terms of the shape-selectivity and unimolecular mechanism for m-cresol as depicted in Scheme 6.1. The observed disproportionation was mainly due to the initial activity on the external surface.

As for o-cresol transformation, disproportionation was enhanced over HBeta and HMordenite due to the non-shape selectivity and wide pores of these zeolites.

6.1.2.2.2 Individual selectivity and p/o-ratio

The selectivity towards p- cresol obtained was 72.5, 21.7 and 48.6% for HZSM5 (Figure 5.12), HBeta (Figure 5.15) and HMordenite (Figure 5.18) respectively, with o-cresol accounting for 20.3, 10.6 and 9.7% respectively of the products. It is evident for the results obtained, that with shape-selective zeolites, like HZSM5, m-cresol is preferable transformed into p-cresol (Scheme 6.1). The reason for the relatively higher (48.6 vs. 21.7%) p-cresol selectivity over HMordenite and HBeta respectively, is probably due to coking, which causes narrowing of the pores resulting in improved shape-selectivity. Although a slight decline in p-cresol selectivity, accompanied by increased o-cresol formation, was observed over HMordenite with increasing m-cresol conversion, these "trends" are in the range of scatter and are therefore questionable in terms of validity.

An initial increase (first hour) in p/o-ratio followed by an immediate decrease was observed over HZSM5 with increasing conversion (Figure 5.13). The p/o-ratio over HBeta changed remarkable (Figure 5.15), which is in contrast to the isomer ratio obtained during the reaction of o-cresol (Section 6.1.1.2.2). Both Figure 5.14 and 5.15 (HBeta) point towards isomerisation via transalkylation. This is explicable in terms of the p-position that is the easiest accessible position on the phenol ring for transalkylation, and hence the increased disproportionation and selectivity towards p-cresol. A decrease in p/o-ratio was observed with increasing conversion over HMordenite (Figure 5.18), which can be attributed to the rapid deactivation of the catalyst.

6.1.3 p-Cresol conversion over zeolites HZSM5, HBeta and HMordenite

p-Cresol was evaluated under the same isomerisation conditions as portrayed for o-cresol.

6.1.3.1 Conversion and activity

After 180 minutes of reaction time, p-cresol conversion of 48.4, 43.5 and 11.0% was correspondingly obtained over HZSM5 (Figure 5.19), HBeta (Figure 5.22) and HMordenite (Figure 5.25). The better conversion over HZSM5 is probably explicable in terms of the activity on the external surface of the catalyst, smaller pores, consecutive reaction (p → m → o) and the unimolecular mechanism as described in section 6.1.1.2. Compared to HBeta and HMordenite, very high m-cresol yield was obtained, while o-cresol and phenol and xylenols were very low for this catalyst.

An increasing amount of disproportionation products were formed with increasing reaction time over HBeta, which is in accordance with o- and m-cresol conversion over this zeolite (Figure 5.4 and 5.13).

An initial increase (first 60 minutes) in the conversion of p-cresol, which thereafter remained constant for the duration of the reaction (Figure 5.25), was observed over HMordenite. This is an indication that the catalyst is deactivating rapidly and hence the lower p-cresol conversion in comparison to HZSM5 and HBeta. From the activity data portrayed in Table 6.3 is it evident that HZSM5 is the most active catalyst followed by HBeta and then HMordenite.

Table 6.3 Activity data deduced from the slopes after 60 minutes of p-cresol conversion in the liquid phase.

	Activity
Catalyst	gcresol/gcat/min
HZSM5	1.104
HBeta*	0.656
HMordenite	0.314

* Data deduced at 120 minutes because no sample was taken at 60 minutes

6.1.3.2 Selectivity

6.1.3.2.1 Isomerisation vs. disproportionation

The selectivity towards isomerisation for the three zeolites tested was proved to be 91.8% (HZSM5, Figure 5.20), 44.4% (HBeta, Figure 5.23) and 71.1% (HMordenite, Figure 5.26) and disproportionation accounted for 9.2, 55.6 and 28.9% respectively. Isomerisation is thus preferred over HZSM5, which is in accordance with o- and m-cresol transformation over HZSM5, while disproportionation is the preferred pathway over HBeta. Although high isomerisation selectivity (71.1%) was obtained over HMordenite, the fact that the catalyst is deactivated after an hour of reaction (Figure 5.25), however, renders this result irrelevant.

6.1.3.2.2 Individual selectivity and m/o-ratio

The individual selectivities for the isomerised (m- and o-cresol) products are illustrated in Figure 5.21 (HZSM5), Figure 5.24 (HBeta) and Figure 5.27 (HMordenite). The selectivity towards m-cresol proved to be 87.2, 42.9 and 58.4%, while o-cresol accounted for 8.33, 1.5 and 12.8% respectively for the three zeolites tested. A slight decrease in o-cresol selectivity was observed with an increase in p-cresol conversion over HZSM5. Since a methyl group cannot easily be transferred to another aromatic ring (unimolecular mechanism for shape-selective zeolites like HZSM5) p-cresol cannot be converted directly to o-cresol[45, 48]. o-Cresol must therefore be regarded as a secondary product, formed via m-cresol, and the increasing m/o-ratio cannot reflect the unimolecular mechanism (Figure 5.21). It is therefore concluded that initially the external surface is still active producing some o-cresol directly from p-cresol through a double transalkylation process and after the external surface is deactivated, a steep increase in m/o-ratio was observed (Figure 5.21). Another probable reason for the steep increase in m/o-ratio could be the fact that m-cresol is thermodynamic more stable than the other two isomers.

m-Cresol selectivity predominates in remarkable manner over HBeta and a decrease (from 49.5-36.5%) with increasing p-cresol conversion was observed

(Figure 5.24). A slight increase in selectivity towards o-cresol and a decrease in m/o-ratio were noticeable for HBeta with increasing conversion.

Although the m- and o-cresol selectivities obtained over HMordenite showed a decline with a slight increase in m/o-ratio as the conversion increased, this result is of little consequence as the catalyst deactivates quickly (*vide supra*).

6.1.4 Comparison of catalysts and cresol isomers

6.1.4.1 Catalyst activity and cresol isomers reactivity

As explained above (refer to section 5.2) trendlines through the origin and the first few data points on conversion vs. reaction time plots have been drawn, whose slopes are taken as an approximate measure of catalyst activity. Tables 6.1 to 6.3 gives the slopes obtained for all the cresol isomers and catalyst tested. Two major trends are observed:

- Average

  Reading of cresol isomers over all the catalysts are identical and follows:

  p-Cresol > o-Cresol ≈ m-Cresol

The ranking does not follow the different intrinsic reactivities of the positions of the methyl groups on the ring towards acid catalysed conversion[51] but rather seems to reflect accessibility of the position in a spaciously restricted environment.

- Activity of catalysts for p-cresol and m-cresol conversion can be rank as follows:

  HZSM > HBeta > HMordenite

But the reverse for o-cresol conversion (no explanation can be given for this ranking).

6.1.4.2 Selectivity of catalysts and cresol isomers

Comparing isomerisation and disproportionation selectivities in detail (see table 6.4) it is evident that isomerisation is largely favoured over zeolite HZSM5 at the expense of disproportionation. This can be explained by disproportionation, which is a bimolecular reaction and therefore involving bulky intermediates (see Scheme 6.2), being largely suppressed in the medium pore channel system of HZSM5.

Over HMordenite, selectivities are almost balanced while HBeta clearly favours disproportionation.

All in all, there is no significant difference or systematic deviation between product selectivities obtained from the different isomers, see table 6.4.

Table 6.4 Isomerisation and disproportionation selectivities of cresol isomerisation over the tested catalysts

	Isomerisation Selectivity (%)		
	o-Cresol	m-Cresol	p-Cresol
HZSM5	66* - 86	93	93 - 92
HBeta	36 - 32	50 - 32	51 - 37
HMordenite	50 – 56	61 - 58	81 - 71
	Disproportionation Selectivity (%)		
HZSM5	34 - 14	7	7 - 8
HBeta	64 - 68	50 - 68	49 - 63
HMordenite	50 - 44	39 - 42	19 - 29

6.2 Continuous vapour phase isomerisation

Given that the isomerisation of the three cresol isomers were performed batch-wise in the liquid phase, the intend of this part of the investigation was to evaluate the isomerisation of o-cresol over zeolites HZSM5, HBeta and HMordenite in the vapour phase in continuous mode. The same space velocity (1.02 hr^{-1}) was used for all three catalysts (refer to revised section 4.2.3, pg 37). The intention and focus of the investigation was the time-on-stream behaviour of the catalysts and a general catalyst screening, not an in depth kinetic analysis.

6.2.1 o-Cresol conversion over zeolites HZSM5, HBeta and HMordenite

6.2.1.1 Conversion and activity

An average o-cresol conversion of 55.8, 18.5 and 18.5% was obtained respectively over HZSM5 (Figure 5.28), HBeta (Figure 5.34) and HMordenite (Figure 5.40) as a function of time-on-stream (TOS).

The results over HZSM5 obtained during the present study show a "quasi steady" state (55.8%) from 24 hours onwards with a very minor, but constant decrease in conversion, while a gradual decline (37.5-8.6% in 93 hours) was observed for HBeta and a rapid decrease (39.5-2.4% in 24 hours) for HMordenite. Despite different operating temperatures (300-600°C for BASF and 380°C for results reported by Imbert), results obtained over HZSM5 during this study compared well with reported values by BASF[38] (65%) and Imbert[52] (~60%), and a decrease in conversion with TOS was also reported by these workers.

The decline in conversion seen for HBeta and HMordenite is in agreement with results reported by Imbert for o-cresol conversion over a wide pore zeolite[40, 52]. The reported decrease (from 40 to <10%), however, was obtained in one hour whilst 93 and 24 hours was needed for HBeta and HMordenite respectively during the current study.

6.2.1.2 Selectivity

6.2.1.2.1 Isomerisation vs. disproportionation

Isomerisation vs. disproportionation selectivity, as a function of TOS, for the three catalysts (HZSM5, HBeta and HMordenite) is depicted in Figures 5.29, 5.35 and 5.41 correspondingly. High isomerisation selectivity (>95%) at conversion of 52-55% was observed for HZSM5, while disproportionation accounted for <5% at the same conversion. At higher conversion (>60%) isomerisation selectivity of ~90% was obtained, while disproportionation accounted for 10% (Figure 5.29). An increase in conversion gave a decrease in isomerisation selectivity as illustrated in Figure 5.29. The initial high disproportionation selectivity of 10% can probably be attributed to activity on the external surface of the catalyst and the higher initial conversion. This result is in accordance with literature[33, 41, 52] where isomerisation selectivity of 90% was found. If we compare the isomerisation to disproportionation (I/D) ratio obtained (10-31, Figure 5.30), a similar trend is reported by Imbert[40, 52] *et.al.* for reaction over HZSM5 (2-10). An increase was observed in I/D ratio as the o-cresol conversion decreased, so at low conversion (~55%) a practically constant I/D selectivity was obtained. The low I/D ratio (~10) obtained at ~60% conversion, confirms the higher selectivity towards disproportionation obtained during this study.

As for HZSM5, HBeta also gave higher disproportionation (57.5%) at high o-cresol conversion (37.5%) whilst low conversion (8.6%) yielded higher isomerisation selectivity (64%, Figure 5.35). An increase in conversion resulted in higher disproportionation selectivity. This is due to the initial activity of the catalyst and the wider pores. A decline in activity was also observed with increasing TOS and this resulted in narrowing pores due to coking. The I/D ratio for HBeta (0.7-1.8) is depicted in Figure 5.36 and is in accordance with literature[41, 52] values (<1.2) reported for wide pore zeolites. It is evident that at conversions $\leq$ 15%, I/D ratio don't change anymore which indicates that the relative rates of the parallel reactions does not change anymore after two days on stream. Due to the declining activity, it still changed for the consecutive reaction (p/m).

The same trend (as with HBeta) with regards to disproportionation and isomerisation selectivity was discernible for HMordenite. At high conversion disproportionation is preferred, while isomerisation is preferred at low conversion (Figure 5.41). This is plausible by means of the initial activity of the zeolite as well as the wider pores that favours disproportionation products. An I/D ratio of <1.0, as a function of conversion, was obtained over HMordenite (Figure 5.42).

6.2.1.2.2 Individual selectivity, p/m- and m/o-ratio

The selectivity towards m- and p-cresol (96.9%) formation over HZSM5 (Figure 5.31), remained constant after one day on stream with m-cresol at 69.7% and p-cresol at 27.2% and an average p/m-ratio of 0.77 (Figure 5.32). While the isomerisation selectivity is in good agreement with reported values of 96.7% (BASF[38], example 15), a difference in p/m-ratio was observed (0.64 vs. 0.77). The equilibrium p/m-ratio reported[52] by Imbert, however, was 0.33 so the p/m-ratio obtained during this investigation proved to be above the equilibrium ratio. Equilibrium m/o-ratio in Imbert's data is almost 1 while the m/o-ratio obtained during the current study approached equilibrium and established it (Figure 5.33).

The cresol isomer distribution (42, 41 and 17% of o-, m- and p-cresol respectively) obtained during this study at 4 hours on stream, however differed completely from that reported[41] as equilibrium values (36, 48 and 16%).

The selectivity towards m- and p-cresol over HBeta showed a decrease with increasing conversion as portrayed in Figure 5.35. Furthermore, a decrease in m-cresol selectivity was discernable with increasing conversion, while p-cresol selectivity remained more or less constant (Figure 5.37). As expected, m-cresol is the dominant product in the m/p-cresol mixture with the highest selectivity for m-cresol (54.5%) and p-cresol (10.1%). The average p/m-ratio obtained was 0.2 and it approaches equilibrium (0.33) as the conversion increases (Figure 5.38). Since this does not reach equilibrium, this reflects kinetic control rather than equilibrium limitations. The consecutive reaction predominates over HBeta and the m/o-ratio (~0.2) obtained (Figure 5.39) was below the equilibrium (1).

The m- and p-cresol selectivity over HMordenite (Figure 5.43) showed a rapid decline with increasing conversion. This is caused by a significant decrease in m-cresol formation (39.4-2.7%), while only a slight decline was noticeable for p-cresol (7.1-1.0%). In fact, m-cresol is only the dominant product in the product mixture at low conversions. As for HBeta, the average p/m-ratio obtained for HMordenite was 0.2 (Figure 5.44). At high conversion, the p/m-ratio approaches equilibrium and at low conversion, the system is still in a kinectically controlled regime. M/o-ratio (0.02) was far below the equilibrium value of 1 and remained constant (Figure 5.45).

7. CONCLUDING REMARKS

The best activity for o-cresol isomerisation, in the liquid phase, was initially HMordenite but because the catalyst deactivates so quickly, HZSM5 was thus regarded as the best catalyst. HZSM5 gave the best activity for both m-cresol and p-cresol isomerisation in the liquid phase. The activity over HBeta was between that of HZSM5 and HMordenite for all the cresol isomer conversions. Expected from the shape selectivity of the zeolite, the best isomerisation selectivity (>86.0%) was obtained with HZSM5. HBeta gave both isomerisation and disproportionation but the preferred pathway is disproportionation, while HMordenite, due to the deactivation, proved to be suitable for neither isomerisation nor disproportionation. It can thus be concluded that HZSM5 gave the best conversion of o-, m- and p-cresol in terms of the desired isomerised product and that it is the preferred catalyst for isomerisation in the liquid phase.

The average activity for o-cresol conversion in the vapour phase followed the order HZSM5 > HBeta ≈ HMordenite. HZSM5 proved to be the best isomerisation catalyst for o-cresol and high selectivity (>95%) and stability was obtained over five days on stream, while HBeta showed a gradual decline in isomerisation selectivity and stability. A rapid decrease was noticeable over HMordenite in terms of selectivity and stability. The activity, stability and isomerisation selectivity data obtained, is therefore conclusive towards HZSM5 being the preferred zeolite for isomerisation of o-cresol.

Further work could entail optimisation of the p-selectivity, from o-cresol and m-cresol transformation, and lifetime studies of the preferred zeolite HZSM5. It is thus recommended to investigate CVD (chemical vapour deposition) to deactivate the external surface of the catalyst as well as noble metal impregnation and/or the use of hydrogen as a carrier gas.

8. REFERENCES

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9. ADDENDUM

Table 1: Results obtained for the batch-wise liquid phase isomerisation of o-cresol over zeolite HZSM5 at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%				
Time (minutes)	40	50	60	120	180
Unknowns < phenol	0.05	0.05	0.05	0.05	0.05
Phenol	0.54	0.56	0.57	0.59	0.71
o-Cresol	96.80	96.48	96.16	95.13	90.10
m-Cresol	1.98	2.28	2.56	3.42	7.41
p-Cresol	0.12	0.14	0.17	0.29	1.14
2,6-Xylenol	0.10	0.09	0.09	0.09	0.09
2,4-Xylenol	0.01	0.01	0.01	0.01	0.02
2,5-Xylenol	0.01	0.01	0.01	0.01	0.03
3,5-Xylenol	0.00	0.00	0.00	0.00	0.01
2,3-Xylenol	0.00	0.00	0.00	0.00	0.01
3,4-Xylenol	0.00	0.00	0.00	0.00	0.00
Unknowns > xylenol	0.39	0.38	0.38	0.39	0.44
Total	100.00	100.00	100.00	99.99	100.00
o-Cresol conversion (mass%)	3.20	3.52	3.84	4.87	9.90
p/m-ratio	0.06	0.06	0.07	0.09	0.15
Equilibrium p/m-ratio	0.33	0.33	0.33	0.33	0.33
Total xylenol + phenols (mass%)	1.10	1.10	1.11	1.15	1.35
Isomerisation Selectivity (mass%)	65.64	68.69	71.16	76.32	86.32
m-Cresol selectivity (mass%)	61.88	64.63	66.72	70.28	74.85
p-Cresol selectivity (mass%)	3.76	4.05	4.44	6.04	11.47
Disproportionation selectivity (mass%)	34.33	31.20	28.86	23.55	13.66

Table 2: Results obtained for the batch-wise liquid phase isomerisation of o-cresol over zeolite HBeta at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%			
Time (minutes)	120	180	240	300
Phenol	2.54	3.39	5.06	5.53
o-Cresol	90.70	88.29	83.75	83.30
m-Cresol	2.63	3.48	4.68	4.69
p-Cresol	0.72	0.55	0.70	0.64
2,6-Xylenol	0.40	0.56	0.79	0.78
2,4-Xylenol	1.04	1.44	1.89	1.88
2,5-Xylenol	0.81	1.21	1.68	1.75
3,5-Xylenol	0.04	0.11	0.17	0.17
2,3-Xylenol	0.23	0.36	0.55	0.55
3,4-Xylenol	0.08	0.04	0.05	0.05
Unknowns	0.80	0.57	0.68	0.65
Total	100.00	100.00	100.00	100.00
o-Cresol conversion (mass%)	9.30	11.71	16.25	16.70
p/m-ratio	0.27	0.16	0.15	0.14
Equilibrium p/m-ratio	0.33	0.33	0.33	0.33
Total xylenol + phenols (mass%)	5.95	7.67	10.88	11.37
Isomerisation Selectivity (mass%)	36.06	34.47	33.06	31.92
m-Cresol selectivity (mass%)	28.31	29.75	28.79	28.08
p-Cresol selectivity (mass%)	7.74	4.72	4.28	3.83
Disproportionation selectivity (mass%)	63.94	65.53	66.94	68.08
o-Cresol conversion (mass%)	0.27	0.16	0.15	0.14

Table 3: Results obtained for the batch-wise liquid phase isomerisation of o-cresol over zeolite HMordenite at 250°, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%		
Time (minutes))	60	120	180
Unknowns < phenol	0.06	0.06	0.05
Phenol	2.07	2.29	1.90
o-Cresol	91.91	91.29	91.12
m-Cresol	2.61	2.77	3.04
p-Cresol	1.25	1.03	1.94
2,6-Xylenol	0.24	0.26	0.22
2,4-Xylenol	0.48	0.57	0.43
2,5-Xylenol	0.64	0.75	0.58
3,5-Xylenol	0.06	0.08	0.05
2,3-Xylenol	0.04	0.05	0.04
3,4-Xylenol	0.00	0.00	0.00
Unknowns > xylenol	0.64	0.86	0.63
Total	100.01	100.00	100.00
o-Cresol conversion (mass%)	8.09	8.71	8.88
p/m-ratio	0.50	0.64	0.48
Equilibrium p/m-ratio	0.33	0.33	0.33
Total xylenol + phenols (mass%)	4.40	3.90	4.23
Isomerisation Selectivity (mass%)	49.46	56.10	47.73
m-Cresol selectivity (mass%)	32.94	34.21	32.30
p-Cresol selectivity (mass%)	16.53	21.89	15.44
Disproportionation selectivity (mass%)	50.52	43.94	52.35

Table 4: Results obtained for the batch-wise liquid phase isomerisation of m-cresol over zeolite HZSM5 at 250°C, 15 atm and 1200 rpm in a 300ml autoclave

	Mass%						
Time (minutes)	40	50	60	80	100	120	150
Unknowns < phenol	0.06	0.06	0.05	0.05	0.05	0.05	0.05
Phenol	0.08	0.09	0.10	0.11	0.12	0.14	0.15
o-Cresol	1.49	1.60	1.76	1.97	2.31	2.76	3.30
m-Cresol	92.75	91.43	90.42	89.36	87.81	85.89	83.73
p-Cresol	5.24	6.39	7.17	7.94	9.08	10.48	11.80
2,6-Xylenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,4-Xylenol	0.01	0.01	0.01	0.01	0.01	0.01	0.01
2,5-Xylenol	0.03	0.03	0.03	0.03	0.03	0.03	0.03
3,5-Xylenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Xylenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4-Xylenol	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Unknowns > xylenol	0.35	0.39	0.46	0.52	0.59	0.64	0.92
Total	100.00	99.99	100.00	100.00	100.01	100.00	100.00
m-Cresol conversion (mass%)	7.25	8.57	9.58	10.64	12.19	14.11	16.27
p/o-ratio	3.53	3.98	4.06	4.03	3.93	3.79	3.57
Equilibrium p/o-ratio	0.32	0.32	0.32	0.32	0.32	0.32	0.32
Total xylenol + phenols (mass%)	0.53	0.57	0.65	0.72	0.81	0.86	1.17
Isomerisation Selectivity (mass%)	92.74	93.24	93.22	93.25	93.40	93.89	92.81
o-Cresol selectivity (mass%)	20.49	18.71	18.41	18.55	18.95	19.60	20.29
p-Cresol selectivity (mass%)	72.25	74.53	74.81	74.70	74.46	74.29	72.52
Disproportionation selectivity (mass%)	7.25	6.68	6.78	6.76	6.65	6.12	7.16

Table 5: Results obtained for the batch-wise liquid phase isomerisation of m-cresol over zeolite HBeta at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%			
Time (minutes)	120	180	240	300
Phenol	0.80	0.75	0.83	0.94
o-Cresol	4.78	1.80	1.36	1.37
m-Cresol	88.82	89.61	88.30	87.06
p-Cresol	1.83	2.45	2.70	2.81
2,6-Xylenol	0.07	0.02	0.01	0.01
2,4-Xylenol	0.16	0.05	0.03	0.03
2,5-Xylenol	0.21	0.09	0.08	0.09
3,5-Xylenol	0.03	0.01	0.01	0.02
2,3-Xylenol	0.06	0.02	0.01	0.02
3,4-Xylenol	0.03	0.02	0.03	0.04
Unknowns	3.21	5.18	6.63	7.62
Total	100.00	100.00	100.00	100.00
m-Cresol conversion (mass%)	11.18	10.39	11.70	12.94
p/o-ratio	0.66	1.12	1.98	2.06
Equilibrium p/o-ratio	0.32	0.32	0.32	0.32
Total xylenol + phenols (mass%)	4.57	6.14	7.64	8.76
Isomerisation Selectivity (mass%)	50.24	40.90	34.70	32.30
o-Cresol selectivity (mass%)	30.27	19.25	11.64	10.56
p-Cresol selectivity (mass%)	19.97	21.64	23.06	21.74
Disproportionation selectivity (mass%)	49.76	59.12	65.30	67.70

Table 6: Results obtained for the batch-wise liquid phase isomerisation of m-cresol over zeolite HMordenite at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%		
Time (minutes)	60	120	180
Unknowns < phenol	0.05	0.06	0.06
Phenol	0.46	0.56	0.64
o-Cresol	0.31	0.41	0.51
m-Cresol	96.14	95.51	94.71
p-Cresol	2.06	2.29	2.57
2,6-Xylenol	0.00	0.00	0.00
2,4-Xylenol	0.00	0.00	0.02
2,5-Xylenol	0.08	0.09	0.11
3,5-Xylenol	0.00	0.00	0.02
2,3-Xylenol	0.00	0.00	0.00
3,4-Xylenol	0.00	0.00	0.00
Unknowns > xylenol	0.90	1.07	1.36
Total	100.00	100.00	100.00
m-Cresol conversion (mass%)	3.86	4.49	5.29
p/o-ratio	6.67	5.59	4.99
Equilibrium p/o-ratio	0.32	0.32	0.32
Total xylenol + phenols (mass%)	1.49	1.78	2.21
Isomerisation Selectivity (mass%)	61.34	60.24	58.33
o-Cresol selectivity (mass%)	7.99	9.15	9.73
p-Cresol selectivity (mass%)	53.35	51.09	48.60
Disproportionation selectivity (mass%)	38.70	39.70	41.74

Table 7: Results obtained for the batch-wise liquid phase isomerisation of p-cresol over zeolite HZSM5 at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%			
Time (minutes)	40	60	120	180
Unknowns < phenol	0.06	0.05	0.05	0.06
Phenol	0.54	0.59	0.67	0.80
o-Cresol	1.97	1.59	1.82	2.44
m-Cresol	19.86	24.55	32.56	42.01
p-Cresol	76.41	71.73	62.67	51.58
2,6-Xylenol	0.01	0.01	0.01	0.01
2,4-Xylenol	0.27	0.27	0.26	0.25
2,5-Xylenol	0.14	0.17	0.22	0.27
3,5-Xylenol	0.04	0.05	0.07	0.10
2,3-Xylenol	0.00	0.01	0.01	0.01
3,4-Xylenol	0.00	0.00	0.00	0.00
Unknowns > xylenol	0.70	0.97	1.65	2.46
Total	100.00	99.99	100.01	99.99
p-Cresol conversion (mass%)	23.59	28.27	37.33	48.42
m/o-ratio	10.11	15.42	17.90	17.21
Equilibrium m/o-ratio	0.95	0.95	0.95	0.95
Total xylenol + phenols (mass%)	1.75	2.12	2.95	3.97
Isomerisation Selectivity (mass%)	92.55	92.48	92.11	91.79
m-Cresol selectivity (mass%)	84.22	86.85	87.24	86.75
o-Cresol selectivity (mass%)	8.33	5.63	4.87	5.04
Disproportionation selectivity (mass%)	7.44	7.50	7.91	8.19

Table 8: Results obtained for the batch-wise liquid phase isomerisation of p-cresol over zeolite HBeta at 250°C, 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%			
Time (minutes)	120	180	240	300
Phenol	4.50	6.18	7.99	10.22
o-Cresol	0.48	0.64	0.86	1.27
m-Cresol	17.93	18.65	19.57	19.52
p-Cresol	63.80	56.55	51.16	43.36
2,6-Xylenol	0.05	0.07	0.10	1.50
2,4-Xylenol	1.71	2.05	2.45	2.94
2,5-Xylenol	1.36	1.84	2.37	3.04
3,5-Xylenol	0.09	0.14	0.20	0.30
2,3-Xylenol	0.34	0.45	0.56	0.71
3,4-Xylenol	0.39	0.56	0.77	1.06
Unknowns	9.34	12.85	13.98	16.08
Total	100.01	100.00	100.00	100.00
p-Cresol conversion (mass%)	36.20	43.45	48.84	56.64
m/o-ratio	37.01	29.02	22.72	15.39
Equilibrium m/o-ratio	0.95	0.95	0.95	0.95
Total xylenol + phenols (mass%)	17.79	24.15	28.41	35.85
Isomerisation Selectivity (mass%)	50.88	44.42	41.82	36.70
m-Cresol selectivity (mass%)	49.54	42.94	40.06	34.46
o-Cresol selectivity (mass%)	1.34	1.48	1.76	2.24
Disproportionation selectivity (mass%)	49.14	55.59	58.17	63.30

Table 9: Results obtained for the batch-wise liquid phase isomerisation of p-cresol over zeolite HMordenite at 250°C, pressure 15 atm and 1200 rpm in a 300ml autoclave.

	Mass%		
Time (minutes))	60	120	180
Unknowns < phenol	0.05	0.05	0.06
Phenol	0.54	0.57	0.63
o-Cresol	2.92	1.65	1.40
m-Cresol	4.50	5.37	6.41
p-Cresol	91.16	91.33	89.02
2,6-Xylenol	0.02	0.00	0.01
2,4-Xylenol	0.18	0.18	0.19
2,5-Xylenol	0.09	0.09	0.10
3,5-Xylenol	0.00	0.00	0.02
2,3-Xylenol	0.00	0.00	0.02
3,4-Xylenol	0.00	0.00	0.00
Unknowns > xylenol	0.54	0.75	2.14
Total	100.00	100.00	100.00
p-Cresol conversion (mass%)	8.84	8.67	10.98
m/o-ratio	3.25	3.68	4.57
Equilibrium m/o-ratio	0.95	0.95	0.95
Total xylenol + phenols (mass%)	1.65	1.72	3.17
Isomerisation Selectivity (mass%)	81.00	80.53	71.14
m-Cresol selectivity (mass%)	61.95	63.33	58.37
o-Cresol selectivity (mass%)	19.05	17.19	12.77
Disproportionation selectivity (mass%)	19.00	19.47	28.84

Table 10: Results obtained for the vapour phase isomerisation of o-cresol over HZSM5 at 350°C, 1 atm. and LHSV = 1.02hr^{-1} in a 10ml fixed-bed reactor.

	Mass%												
Time (hours)	4	20	24	51	73	93	95	97	99	101	106	117	121
Unknowns < phenol	0.12	0.05	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0	0	0.02
Phenol	2.26	2.70	1.41	1.07	0.98	0.94	0.94	0.89	0.88	0.87	0.84	0.77	0.79
o-Cresol	39.94	39.20	44.02	44.82	46.28	46.37	46.41	46.62	46.87	47.02	46.26	47.18	46.88
2,6-Xylenol	0.27	0.36	0.20	0.15	0.14	0.13	0.13	0.13	0.13	0.13	0.11	0.11	0.11
p-Cresol	15.89	15.60	15.05	15.02	14.57	14.72	14.69	14.52	14.43	14.42	14.73	14.37	14.54
m-Cresol	39.03	38.90	37.81	37.87	37.06	36.96	36.95	36.99	36.85	36.74	37.28	36.86	36.92
2,4-Xylenol	0.64	0.83	0.43	0.33	0.30	0.28	0.28	0.27	0.27	0.26	0.25	0.23	0.24
2,5-Xylenol	0.88	1.15	0.60	0.46	0.42	0.39	0.39	0.38	0.37	0.37	0.35	0.32	0.33
2,3-Xylenol	0.20	0.26	0.13	0.09	0.08	0.07	0.07	0.07	0.06	0.06	0.05	0.05	0.05
3,5-Xylenol	0.05	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3,4-Xylenol	0.35	0.47	0.23	0.18	0.16	0.15	0.14	0.14	0.14	0.13	0.12	0.11	0.12
Unknowns > phenol	0.36	0.40	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
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
o-Cresol conversion (mass%)	60.06	60.80	55.98	55.18	53.72	53.63	53.59	53.38	53.13	52.98	53.74	52.82	53.12
p/m-ratio	0.41	0.40	0.40	0.40	0.39	0.40	0.40	0.39	0.39	0.39	0.40	0.39	0.39
Equilibrium p/m-ratio	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Total xylenol + phenols (mass%)	5.14	6.29	3.12	2.28	2.09	1.96	1.95	1.87	1.85	1.82	1.73	1.59	1.66
Isomerisation Selectivity (mass%)	91.45	89.66	94.43	95.86	96.11	96.35	96.37	96.49	96.52	96.56	96.79	96.98	96.88
m-Cresol selectivity (mass%)	64.99	63.99	67.54	68.53	68.98	68.91	68.95	69.29	69.36	69.35	69.38	69.79	69.51
p-Cresol selectivity (mass%)	26.46	25.67	26.89	27.23	27.12	27.44	27.41	27.20	27.16	27.21	27.41	27.20	27.37
Disproportionation selectivity (mass%)	8.55	10.34	5.57	4.14	3.89	3.65	3.63	3.51	3.48	3.44	3.21	3.02	3.12
I/D-ratio	10.69	8.67	16.95	23.16	24.68	26.37	26.52	27.52	27.76	28.05	30.14	32.14	31.03

Table 11: Results obtained for the vapour phase isomerisation of o-cresol over zeolite HBeta at 350°C, 1 atm. and LHSV = 1.02hr^{-1} in a 10ml fixed-bed reactor.

	Mass%													
Time (hours)	4	8	18	22	26	44	46	48	51	56	68	71	91	93
Unknowns < phenol	0.38	0.44	0.07	0.05	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0	
Phenol	10.36	7.66	4.81	4.41	4.10	2.78	2.81	2.67	2.48	2.38	2.03	1.93	1.60	1.41
o-Cresol	62.46	68.74	75.38	77.07	78.65	83.35	83.63	84.25	84.81	85.69	87.69	88.22	90.27	91.37
m-Cresol	12.99	12.22	11.82	11.09	10.73	8.81	8.63	8.42	8.14	7.76	6.71	6.43	5.30	4.70
p-Cresol	2.96	2.73	2.50	2.31	2.18	1.69	1.65	1.59	1.52	1.43	1.19	1.13	0.87	0.82
2,6-Xylenol	1.28	1.05	0.74	0.68	0.64	0.50	0.49	0.47	0.47	0.44	0.40	0.39	0.35	0.32
2,4-Xylenol	2.64	2.13	1.48	1.39	0.02	1.01	1.01	0.95	0.94	0.88	0.81	0.79	0.70	0.60
2,5-Xylenol	2.53	2.15	1.56	1.44	1.33	0.97	0.94	0.90	0.88	0.81	0.69	0.66	0.55	0.47
3,5-Xylenol	0.97	0.59	0.40	0.36	0.33	0.23	0.22	0.20	0.19	0.16	0.12	0.11	0.07	0.07
2,3-Xylenol	0.86	0.71	0.50	0.45	0.41	0.28	0.27	0.25	0.24	0.22	0.18	0.17	0.13	0.12
3,4-Xylenol	0.71	0.06	0.02	0.03	0.03	0.22	0.21	0.19	0.19	0.17	0.13	0.13	0.09	0.09
Unknowns > greater than xylenols	1.85	1.52	0.73	0.73	1.54	0.16	0.13	0.10	0.13	0.05	0.02	0.03	0.05	0.02
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
o-Cresol conversion (mass%)	37.54	31.26	24.62	22.93	21.35	16.65	16.37	15.75	15.19	14.31	12.31	11.78	9.73	8.63
p/m-ratio	0.23	0.22	0.21	0.21	0.20	0.19	0.19	0.19	0.19	0.18	0.18	0.18	0.16	0.17
Equilibrium p/m-ratio	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Total xylenol + phenols (mass%)	21.58	16.31	10.30	9.53	8.44	6.15	6.09	5.74	5.52	5.12	4.40	4.23	3.55	3.11
Isomerisation Selectivity (mass%)	42.50	47.82	58.16	58.43	60.46	63.03	62.76	63.55	63.62	64.24	64.21	64.12	63.48	63.99
m-Cresol selectivity (mass%)	34.62	39.08	48.02	48.38	50.24	52.90	52.71	53.44	53.60	54.25	54.52	54.53	54.54	54.47
p-Cresol selectivity (mass%)	7.88	8.74	10.14	10.06	10.22	10.13	10.05	10.11	10.03	9.99	9.69	9.59	8.94	9.51
Disproportionation selectivity (mass%)	57.50	52.18	41.84	41.57	39.54	36.97	37.24	36.45	36.38	35.76	35.79	35.88	36.52	36.01
I/D-ratio	0.74	0.92	1.39	1.41	1.53	1.70	1.69	1.74	1.75	1.80	1.79	1.79	1.74	1.78

Table 12: Results obtained for the vapour phase isomerisation of o-cresol over zeolite HMordenite at 350°C, 1 atm. and LHSV = 1.02hr^{-1} in a 10ml fixed-bed reactor.

	Mass %		
Time (hours)	2	18	24
Unknowns < phenol	26.53	8.12	0.82
Phenol	8.81	2.35	0.36
o-Cresol	60.49	86.54	97.59
2,6-Xylenol	0.03	0.07	0.03
p-Cresol	0.30	0.43	0.17
m-Cresol	1.07	1.86	0.95
2,4-Xylenol	0.67	0.14	0.05
2,5-Xylenol	0.04	0.13	0.02
2,3-Xylenol	0.83	0.06	
3,5-Xylenol	0.03	0.07	
3,4-Xylenol	0.03	0.02	
Unknowns > phenol	1.16	0.21	
Total	100.00	100.00	100.00
o-Cresol conversion (mass%)	39.51	13.46	2.41
p/m-ratio	0.28	0.23	0.18
Equilibrium p/m-ratio	0.33	0.33	0.33
Total xylenol + phenol + lower than phenol	38.14	11.17	1.29
Isomerisation Selectivity (%)	3.47	17.01	46.56
m-cresol selectivity	2.72	13.84	39.41
p-cresol selectivity	0.75	3.17	7.15
Disproportionation Selectivity	96.53	82.99	53.44
I/D ratio	0.04	0.20	0.87