

**The rate inhibiting effect of water as a product on reactions
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Formation of mesityl oxide from acetone as a case study

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[University of Pretoria etd – Du Toit, E.L. \(2003\)](#)

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by

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Submitted in partial fulfilment of the requirements for the degree

M. Eng (Chemical)

in the

Faculty of Engineering, the Built Environment and Information Technology

University of Pretoria

Pretoria

2003

Synopsis

The rate inhibiting effect of water as a product on reactions catalysed by cation exchange resins:

Formation of mesityl oxide from acetone as a case study

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It is known that when water is a product in reactions catalysed by cation exchange resins, it inhibits the reaction rate much more than predicted by the reverse reaction or dilution effects. In this work the inhibiting effect is ascribed to the preferential association of the catalytically active sites with water. In the derivation of the kinetic model, a Freundlich type adsorption isotherm was used to quantify the number of sites occupied by water. This is combined with a power law expression for the reaction rate. The resultant expression can accurately predict the reaction rate for various initial concentrations of water and mesityl oxide. Even when water was initially added to the reaction mixture, this model still gave an absolute average error of 6.5% compared to a 54.6% error when the same approach was followed but with the more popular Langmuir isotherm to describe site deactivation. The kinetic expression previously proposed for this reaction system by Klein and Banchero also failed when water was added to the reaction mixture and gave

an average error of 71.1%. The procedure used to derive the model is therefore suggested for all cation exchange catalysed reactions where water is one of the products.

KEYWORDS: cation exchange resins, catalysis, adsorption, Freundlich isotherm, kinetics, modelling, mesityl oxide, acetone, rate inhibition, power law

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Nomenclature list

Symbols used

a_i	Activity of component i	mol/cm ³
C_A	Concentration of A	kmol/m ³
D_A	Molecular diffusion coefficient of component A	m ² /s
D_e	Effective diffusivity	m ² /s
d_p	Particle diameter	m
J_{AB}	Intraparticle diffusional flux	kmol/m.s
K_A	Adsorption constant in Freundlich model	l/mol
K_{eq}	Reaction equilibrium constant	-
K_{KB}	Rate constant in Klein & Banchero's model	l ² /mol ²
K_{si}	Adsorption equilibrium constant for component i	-
K_w	Water inhibition coefficient in Yang's model	l ² /mol ²
k	Reaction rate constant	1/s or 1/eq.s, or l ² /mol.min.eq
k_c	Mass transfer coefficient	m/s
k_{eff}	Global reaction rate coefficient	1/eq.s
M	Molecular weight	g/mol
r	Reaction rate related to the total number of sulphonic acid groups	mol/s.eq or mol/min.eq
r''	Reaction rate in terms of catalyst surface area	mol/s.m ²
r'	Reaction rate in terms of catalyst mass	mol/s.g
R	Resin particle radius	m

T	Temperature	K
V	Molecular volume at normal boiling point	cm ³ /gmol
w	Amount of solute adsorbed per unit mass - adsorbent	-

Greek Symbols

α	Constant in Freundlich model	K ⁻¹
ϵ	Bed porosity	-
ϵ_p	Pellet porosity	-
ϕ	Thiele modulus	-
Φ_{WP}	Weisz or Weisz Prater modulus	-
η	Internal effectiveness factor	-
$\eta(H_2O)$	Effectiveness factor to incorporate inhibiting effect of water in Limbeck's model	-
μ	Viscosity	in Eq 26, cP
θ	Fraction of occupied adsorbent sites	-
θ_A	Number of sites occupied by A	-
θ_V	Number of vacant sites	-
ρ_c	Catalyst density	g/m ³
σ	Catalyst constriction factor	-
τ	Catalyst tortuosity	-

Abbreviations

Ac	Acetone
BD	Butanediol
ETBE	Ethyl <i>tert</i> -butyl ether
EtOH	Ethanol
eq	Number of equivalent acid groups
GC	Gas chromatograph
IB	Isobutene
MSO	Mesityl Oxide
TBA	<i>tert</i> -butyl alcohol
THF	Tetrahydrofuran

Subscripts

ads	adsorption
b	bulk phase (concentration)
des	desorption
eq	equilibrium
0	initial conditions
obs	observed
ov	overall
s	at the catalyst surface

1. Introduction

During the past few decades, solid acid catalysts replaced most of their homogeneous counterparts in industrial scale acid catalysed reactions. Increased environmental accountability of chemical companies and the always-present drive for more efficient processes are the major driving forces behind this transition. The two main advantages of solid acid catalysis in this respect is the ease of separation of the solid catalysts from the reaction mixture and the fact that their selectivity and activity are often much better compared to that of homogeneous acid catalysts (Tanabe and Hölderich, 1999). Both these aspects will lead to a reduction in the amount of waste produced thus moving closer to the ultimate goal of zero waste production. Cation exchange resins play a key, although not exclusive, role in this rapidly growing area (Harmer and Sun, 2001).

Accurate modelling of the reaction rate is normally regarded as an essential tool in the design of reaction equipment. It is therefore important to be able to formulate the kinetic description for reactions catalysed by cation exchange resins. Knowledge of the reaction kinetics can further be used in the design and manufacture of even more efficient catalysts based on the behaviour of a specific reaction system (Levenspiel, 1999).

Many researchers have confirmed the potentially complicated nature of the rate of reactions catalysed by cation exchange resins. (Buttersack, Widdecke and Klein, 1986; Ihm, Ahn and Jo, 1996; Rehfinger and Hoffmann 1990a, 1990b; Schwarzer, Horst , Kunz and Hoffmann, 2000; Tejero, Cunhill, Iborra, Fit  and Parra, 1996; Yadav and Kulkarni, 2000; Yadav and Thatagar, 2002; Yang, Yang and Yao, 2000) Their work shows that the rate may be affected by mass-transfer phenomena as well as preferential adsorption of some of the reactants or products – both effects depending on the specific reaction system under investigation.

In organic liquid phase reactions where water is present in the mixture, another dimension is added to the behaviour of the system (Sharma, 1995).

This is especially relevant where water is one of the reaction products. In these systems water has a detrimental effect on the reaction rate (Chakrabarti and Sharma, 1993; Gates, 1992: 187-195). In order to describe the reaction rate of such systems, researchers use empirical inhibition factors for water, or limit their investigation to specific concentration ranges (Limbeck, Altwicker, Kunz, and Hoffmann, 2001; Yang *et al.*, 2000; Kawase, Inoue, Araki and Hashimoto, 1999).

The aim of this study is to quantify the rate inhibition effect of water in a temperature dependant kinetic expression. Such a rate expression should be applicable over a wide concentration range and should be able to describe the rate for varying initial concentrations of reactants and products. In addition, the derivation of the model should preferably be based on fundamental theories and not be of an empirical nature. It is then hoped that it is possible to propose a generic approach that is applicable to other similar reaction systems.

The condensation reaction where mesityl oxide (MSO) and water are formed from acetone over a cation exchange resins was studied as a representative of reaction systems where water is a reaction product. This reaction was studied in a batch reactor at different temperatures and with varying initial concentrations of products and the reactant.

2. Theory

2.1. Cation exchange resins

Cation exchange resins consist of a matrix of a crosslinked polymer with fixed anionic groups, which are responsible for a negative surplus charge. This surplus charge is balanced by cations referred to as counter ions. The counter ions (cations) are free to move within the framework and in the case of ion exchange can be replaced by other cations (Helfferich, 1962: 5-16). In most applications where cation exchange resins are used as catalysts, SO_3^- ions give the negative charge and the counter ions are H^+ ions – which are the catalytically active groups (Chakrabarti and Sharma, 1993).

Ion exchange resins can be divided into two groups: gel resins and macroreticular resins. The gel resins have a homogeneous three-dimensional matrix with no discontinuities, while macroreticular resins are two-phased structures consisting of macropores and gellular microspheres. Macroreticular resins are preferred in the case of catalysis due to their permanent pores and increased active surface area (Abrams and Millar, 1997).

2.1.1. Gellular ion exchange resins

A resin gel can be formed by the polymerisation of vinyl monomers. The resultant resin should be a robust solid that is insoluble in solvents. In order to achieve the desired physical properties, the vinyl monomer is copolymerised with a closely related bifunctional monomer, which acts as a crosslinking agent (Gates, 1992: 183). Most important resins of this type are formed from the copolymerisation of styrene with divinylbenzene (DVB) as crosslinking agent (Chakrabarti and Sharma, 1993). Figure 1 gives an illustration of this copolymerisation process. The result is a three-dimensional crosslinked matrix of hydrocarbon chains. The chemical characteristics of the polymer molecules are almost identical to that of the linear polystyrene, but physically the polymer structure is much more rigid.

Cation exchange resins can be prepared from monomeric organic electrolytes, in which case the catalytic groups ($\text{-SO}_3\text{H}^+$) are already part of the matrix after polymerisation and the matrix does not require to be functionalised. However, present day cation exchange resins are prepared from addition polymerisation of non-ionic monomers. The resin is only “activated” with concentrated sulphuric acid after polymerisation. In order to prevent the resin to crack due to the severe strain on the matrix during the sulphonation, the beads are allowed to swell in a suitable polar solvent. Complete monosulphonation of all benzene rings, including those of divinylstyrene, will result if sufficient reaction time is allowed. Figure 2 gives a schematic representation of the sulphonation process.

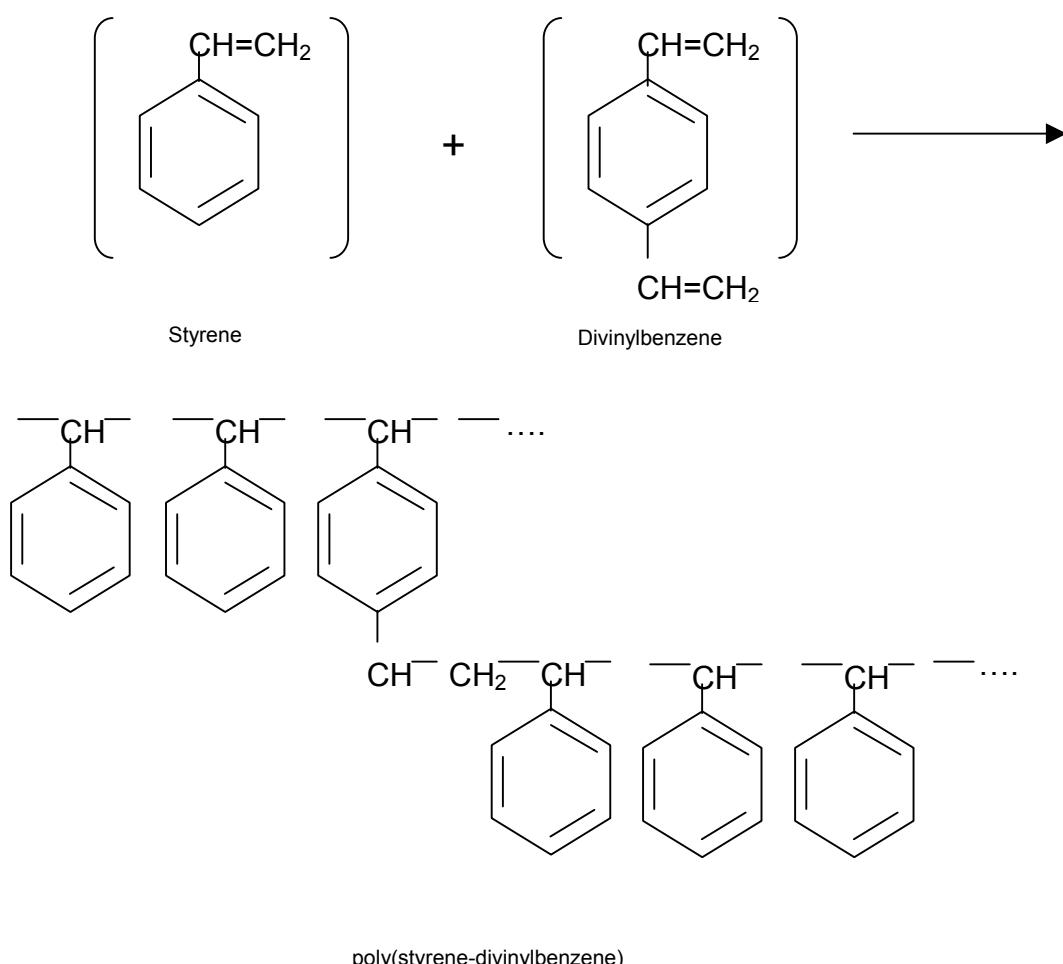


Figure 1: The copolymerisation of styrene and divinylbenzene

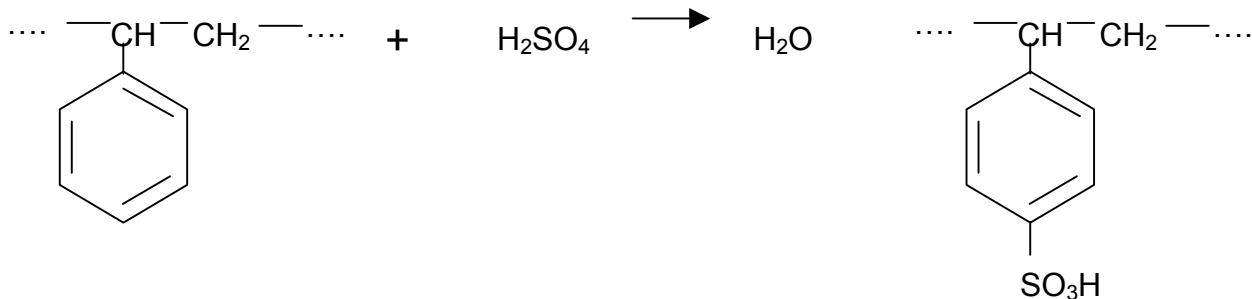


Figure 2: The sulphonation process

Due to the crosslinking between hydrocarbon chains in ion exchange resins, each resin particle is practically one single insoluble macromolecule. Gellular resins do not have permanent pores. Instead, these resins depend on a polar solvent, which causes the matrix to swell, for pores to be established. Swelling of the resin matrix can be explained by realising that the sulphonic groups in the matrix have an affinity for polar solvent molecules and tend to surround themselves with such molecules if they are present (Helfferich, 1962: 100-101). Monomers with sulphonic groups would be soluble in polar solvents. In the cationic exchange resin, this “dissolution” process gets under way, driven by the affinity of the sulphonic groups for the polar solvent. The coiled and packed chains of the matrix “unfold” in order to make room for the solvent molecules. The crosslinking of the chains, however, prevent them from being separated completely – as a result the resins swell, but do not dissolve. The resultant pore dimensions then depend on the properties of the solvent employed as well as the degree of crosslinking. In the dried form (in the absence of a solvent) the pores “collapse” and the polystyrene chains will be as close as atomic forces allow (Chakrabarti and Sharma, 1993). In this state, no internal catalytic surface area is available.

The fact that a polar solvent needs to be present for the internal surface area to be available for catalysis, limits the amount of systems where the resin can be utilised as catalyst to systems with a polar solvent or reactant. This conventional polymerisation technique can however easily be modified to yield

the highly porous, so-called macroreticular or macroporous ion exchange resins.

2.1.2. Macroporous resins

The development of macroporous – also called macroreticular - resins made it possible to use ion exchange resins as catalysts even in non-swelling media. This is due to the availability of active sites within permanent, relatively rigid pores (Chakrabarti and Sharma, 1993).

The preparation of macroporous ion exchange resins involve the presence of an inert organic, which is a good solvent for the monomer but a poor solvent for the polymer, during the copolymerisation process (Abrams and Millar, 1997). This brings about precipitation during the polymerisation, where the solvent remains inside the liquid globules of monomer mixture during suspension polymerisation. The solvent is removed after polymerisation leaving behind a resin with permanent, relatively rigid pores.

The macroreticular resin can now be envisaged as two phases, i.e. the agglomeration of very small gellular microspheres of uniform size and the macropore formed by the space between the microspheres (Harmer and Sun, 2001, Satterfield, 1970: 149, Ihm *et al.*, 1996). The geometry of a macroporous resin is shown in figure 3.

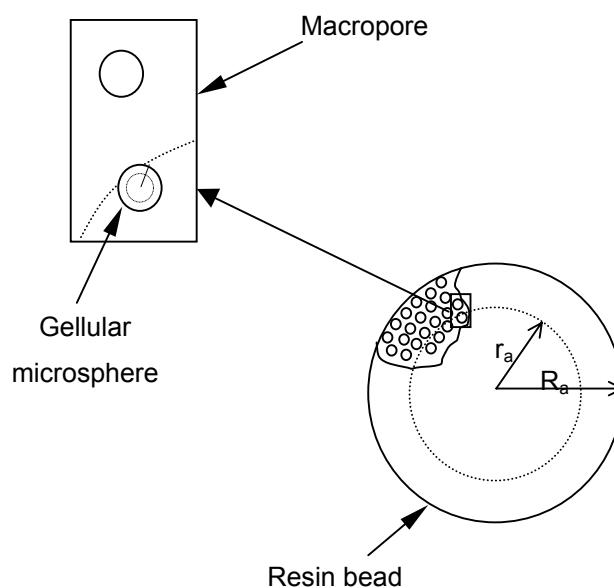


Figure 3: Presentation of the structure of a macroporous resin catalyst bead

Reactants can move easily into the interior of the bead through the macropores – even in the case of a non-swelling reaction medium. The active sites are now exposed on the surface of the macropores rather than buried in a tangle of hydrocarbon chains. This porous polymer bead may have 100 times as much active surface area as the gellular bead, which has only the external area in a non-swelling agent (Gates, 1992: 221).

In a polar medium the gel phase microspheres of the resin will swell. This will result in the formation of micropores through which reactants and products can come into contact with even more of the catalytically active sites. The fraction of the total number of active sites that is located in the micropore depends on the degree of crosslinking and porosity of the resin. According to Ihm *et al.* (1996) less than 5% of the active sites (-SO₃H groups) in the case of the commercially available Amberlyst®15 resin is located on the surface of the microsphere (i.e. in the macropore). The remaining functional groups are located within the polymer matrix or gel of the microsphere. With Aberlyst®XN-1010, which has a much higher degree of crosslinking, almost 53% of the -SO₃H groups are located on the surface of the gellular microspheres.

2.2. Rate determining steps during catalysis with cation exchange resins

The principle difference between catalysis by homogeneous catalysts and by resins (beside the obvious mechanical benefits) is that with resins catalysis overlaps with diffusion, adsorption and desorption processes. These effects depend on the nature of the matrix, the reactant system and the solvents used (if any) in the reaction.

In order for the reaction to occur, the reactants must get to the active sites and the products must be removed. The different steps that may have an influence on the reaction rate are therefore analogous to those of any heterogeneously catalysed reaction. Fogler summarises them as follows (1999, 592):

- Mass transfer of the reactants from the bulk fluid to the external surface of the resin pellet
- Diffusion of reactant from the pore mouth through the resin pores to the immediate vicinity of the counter ions (in this case cations)
- The catalysed chemical reaction itself (referred to as the surface reaction)
- Diffusion of products from the interior of the resin to the external surface
- Mass transfer of products from the external resin bead to the bulk fluid

In order to predict the rate of a resin-catalysed reaction, one needs to determine which of these steps (or combination of steps) controls the reaction rate. The different rate controlling steps can be further complicated by the matrix structure of the specific resin as well as its behaviour in the particular reaction mixture of interest. The rate of a resin-catalysed reaction will be a function of the acidity as well as the accessibility of the sites. The acidity is a function of the type and number of acid groups on the polymer matrix, degree of crosslinking as well as the reaction medium. Accessibility is a function of the degree of crosslinking, particle size, porosity, reaction medium, diffusivity of reactants and products (Chakrabarti and Sharma, 1993). In the subsequent sections, the possible rate-controlling steps and their application in resin catalysis are grouped into three sections, namely:

- The surface reaction (including the influences of adsorption and desorption)
- Internal mass transfer (diffusion)
- External mass transfer

It should be noted that a temperature gradient might exist within the porous particle, which may also influence the rate of the overall reaction. In the same manner, a temperature gradient can exist across the external film. In liquid systems these phenomena rarely influence the rate of the reaction

(Levenspiel, 1999: 378). The following discussion does therefore not take the effect of temperature gradients within the reaction mixture into consideration.

2.2.1. Rate of the surface reaction

In heterogeneous catalysis, adsorption of reactants, chemical reaction and desorption of the products are steps that occur in series and all are grouped together under the term surface reaction (Gates, 1992: 187).

Levenspiel (1999:380) strongly recommends that the simplest approach – even if this implies that the approach is empirical – should be followed when a rate expression for the surface reaction is developed. He mentions that most catalytic conversion data can be fitted adequately by relatively simple first- or nth order rate expressions and that these expressions are good enough for engineering purposes. However, many researchers on cation exchange resin catalysis found that simple nth order rate expressions came nowhere close to describing the experimental data and that the adsorption/desorption effects need to be included in the rate expressions (Rehfinger and Hoffmann, 1990a; Sola, Pericas, Cunhill and Tejero, 1995; Fit , Iborra, Tejero and Izquierdo, 1994; Limbeck, Altwicker, Kunz and Hoffmann, 2001; Rihko-Struckmann, Latostenmaa, and Krause, 2001).

Researchers in the field of resin catalysis use either a pseudo-homogeneous or a pseudo-heterogeneous approach to describe liquid phase surface reactions.

The pseudo-homogeneous approach

The pseudo-homogeneous model is based on the theory suggested by Helfferich (1962:523) that the counter ions (mostly H^+ in the case of cation exchange resins) are mobile and solvated and thus in a condition which is, in principle, not different from that in a corresponding homogeneous solution. The reaction mechanism in homogeneous catalysis by a dissolved electrolyte and heterogeneous catalysis by a resin is then essentially the same and the only difference between homogeneous and heterogeneous catalysis is the internal and external diffusion processes.

The idealised homogeneous case requires complete swelling of the matrix. In the presence of polar compounds, solvation of the polymer-bound $\text{--SO}_3\text{H}$ takes place. This means that the $\text{--SO}_3\text{H}$ group are totally dissociated. The H^+ ions can move freely in the liquid within the pores and act as the active centres while the --SO_3^- ions remain fixed on the polymer surface. The reaction mechanism is assumed to be the same as the one observed with the dissolved electrolyte, but confined to the liquid within the catalyst mass. This approach is particularly applicable in cases where the reactants or the reaction solvent is strongly polar (Saha, 1999; Khan and Rahman, 1996). It also proved successful in studies where excessive quantities of the more polar reactant in the system were used (Yadav and Kulkarni, 2000; Yadav and Thathagar, 2002).

The negatively charged polymer, although not directly involved in the catalytic activation of the substrate, now forms a special microenvironment for the catalytically active centres (Tejero *et al.*, 1996). The actual concentration of the different components of the reaction mixture in the resin phase may not be the same as that in the bulk solution – even in the absence of any mass transfer effects. There may be preferential distribution of some of the components depending on their relative compatibility with the resin phase microenvironment due to the preferential association of specific molecules with the negatively charged matrix. This complicates the model, as a distribution coefficient needs to be determined for each component in order to calculate the concentrations inside the resin pores. Chakrabarti and Sharma (1993) suggest experimental methods for doing this. The term quasi- or pseudo-homogeneous therefore suitably designates this type of catalysis.

The pseudo-heterogeneous approach

If the reaction medium is not sufficiently polar, the $\text{--SO}_3\text{H}$ groups remain undissociated. In this case a simple homogeneous model may not fit the data adequately (Chakrabarti and Sharma, 1993) and a pseudo-heterogeneous approach is suggested.

The idealised heterogeneous state is characterised by a direct interaction of the reactants with the polymer fixed acid. The degree of adsorption is limited by the fraction of accessible groups on the surface of the polymer. The exclusive interaction of the substrate with the surface requires a very hard, highly crosslinked polymer and the absence of swelling. However in the real situation swelling cannot be completely excluded. Therefore the term quasi- or pseudo-heterogeneous catalysis is appropriate. In this case the catalytic agent is the sulphonic group itself, and from a molecular point of view the reactions occur by concerted cyclical mechanisms with proton transfer (Tejero *et al*, 1996). Researchers in resin catalysis use adsorption and desorption processes to model this behaviour. In most cases, this approach is based on a Langmuir-Hinshelwood or Eley-Rideal mechanism. These models account for adsorption of reactants and products based on different scenarios (Fogler, 1999: 600).

Langmuir-Hinshelwood mechanism

This term is generally applied when the rate-determining step in a reaction involves only adsorbed reactants – or in this case reactants associated with the fixed $-SO_3H$ groups. For this analysis to hold true, it is also assumed that the Langmuir adsorption isotherm accurately describes the fraction of adsorption/active sites occupied by each reactant at adsorption equilibrium (Gates, 1992: 195-204). The main assumptions underlying the Langmuir adsorption model are that:

- All adsorption sites are equivalent
- Interactions between molecules bonded to these sites are negligible
- Only one adsorbing molecule can be bonded to each site on the solid (Atkins, 1990:885)

If the adsorption of reactant A is considered, the rate of adsorption is proportional to the concentration of A in the surrounding fluid (C_A) as well as the fraction of vacant adsorption sites (θ_v):

The rate of desorption of A is then expected to be proportional to the number of sites occupied by A (θ_A):

$$r_{des} = k'\theta_A \dots \quad (2)$$

At equilibrium the two rates are equal. With $\theta_v + \theta_A = 1$ and if k/k' is defined as $K_{S,A}$ the adsorption equilibrium constant of component A, equation 3 is obtained:

$$\theta_A = \frac{K_{S,A} C_A}{1 + K_{S,A} C_A} \dots \quad (3)$$

In the same manner it can be shown that if adsorption of two species A and B occurs simultaneously on the sites:

$$\theta_A = \frac{K_{S,A} C_A}{1 + K_{S,A} C_A + K_{S,B} C_B} \dots \quad (4)$$

and

$$\theta_B = \frac{K_{S,B} C_B}{1 + K_{S,A} C_A + K_{S,B} C_B} \dots \quad (5)$$

In the situation where all the reactants (A and B in this case) are in the adsorbed phase when the reaction occurs, it can be expected that the reaction rate will be second-order in the extent of surface cover (Atkins, 1990: 897):

$$r = k\theta_A \theta_B \dots \quad (6)$$

If both reactants follow Langmuir adsorption isotherms and adsorb without dissociation the rate law is given by equation 7:

$$r = \frac{k K_{sA} C_A K_{sB} C_B}{(1 + K_{sA} C_A + K_{sB} C_B)^2} \dots \dots \dots \quad (7)$$

In this pseudo-heterogeneous case, where the fixed $-SO_3H$ groups act as the active centres, components that do not participate in the reaction may also be adsorbed on the resin. The number of available active sites will be reduced and the reaction rate will be influenced (Gates, 1992: 201). For example, in a reaction system where two molecules of A reacts in a medium where small amounts of component W - which also adsorb on the active groups - are present, component W will compete for the active $-SO_3H$ groups in the resin.

With the following reaction kinetics:

and adsorption equilibrium described by:

$$\theta_A = \frac{K_{sA} C_A}{1 + K_{sA} C_A + K_{sW} C_W} \dots \quad (9)$$

The resultant Langmuir-Hinshelwood rate expression is:

The described approach, as well as knowledge of preferential adsorption of some of the reactants and products in order to determine equilibrium adsorption constants, is successfully used to describe some resin-catalysed

reactions (Rehfinger and Hoffmann, 1990a; Oktar, Kirali, Timur, Dogu and Dogu, 1999).

The Eley-Rideal Mechanism

In this mechanism an unabsorbed molecule collides and reacts with adsorbed molecules of another reactant (Atkins, 1990: 895). The model therefore predicts that the reaction rate will be first order in terms of surface coverage of the catalyst.

In the case of the reaction: A + B → C,

$$r = kC_B\theta_A \dots \quad (11)$$

If the Langmuir adsorption isotherm is still assumed to describe equilibrium adsorption of the adsorbed molecule, the surface reaction rate will be:

$$r = \frac{kK_{S,A} C_A C_B}{1 + K_{S,A} C_A} \dots \quad (12)$$

In systems where this model is used to describe the surface reaction, the more polar reactant is seen to “adsorb” on the active sites and react with the other reactants in the pore liquid. In most resin-catalysed reactions where a pseudo-heterogeneous approach is followed, the Eley-Rideal model seems to be more suitable than the Langmuir-Hinshelwood model (Rihko-Stuckmann, *et al.*, 2001; Schwarzer *et al.*, 2000; Sola *et al.*, 1995; Fit   et al., 1994; Buttersack *et al.*, 1986).

2.2.2. External Diffusion (Film diffusion)

When a fluid passes over the surface of a pellet, a laminar layer is developed in which the velocity parallel to the surface varies rapidly over a very short distance normal to the flow. The fluid velocity is zero at the solid surface, but approaches the bulk-stream velocity at a plane not far from the surface (usually less than 1mm). In the bulk fluid stream, product and reactants are

mixed and transported at rates that depend primarily on the nature of the flow. Near the pellet surface however, the fluid velocity is low and there is little mixing (Satterfield, 1970:79). This results in an essentially stagnant boundary layer. The thickness of this boundary layer is highly dependant on the velocity of the fluid past the particle. In the bulk fluid, the transport is independent of diffusion, but near the catalyst surface the transport rate is proportional to the concentration gradient over the boundary layer and the molecular diffusion coefficient (Gates, 1992:240-241). The transport of products and reactants normal to the catalyst surface are therefore by molecular diffusion over this stagnant boundary layer. For a very active catalyst, i.e. when the surface reaction rate is very fast, the overall reaction rate may be determined by how fast the reactants diffuse through the boundary layer.

According to Helfferich (1962:547) and Chakrabarti and Sharma (1993) film diffusion control is comparatively rare in cation exchange resin catalysed reactions since film diffusion is a rather fast process. The problem with lab scale reactions, however, is that residence times comparable to industrial situations may lead to very low fluid velocities and therefore a thicker laminar boundary layer. It is therefore important to ensure that experimental studies are in areas free of external mass transfer (Fogler, 1999: 699).

There are two experimental approaches to determine whether film diffusion influences the overall reaction rate. The first is based on the fact that if external mass transfer limits the reaction, the observed reaction rate will depend on the fluid velocity past the particle. In a slurry reactor, the reaction rate should therefore be independent of the agitation speed if no film diffusion effects are present. In a fixed bed reactor, a change in the superficial velocity (at the same residence time) would have no impact on the rate if external mass transfer can be neglected. Most researchers using cation exchange resins found that it is possible to exclude external mass transfer effects by operating at adequate agitation speeds in stirred reactors or by increasing the experimental superficial velocity in packed bed reactors (Chopade and Sharma, 1996; Kawase *et al.*, 1999;; Limbeck *et al.*, 2001; Rehfinger and

Hoffmann, 1990a and 1990b; Klein and Banchero, 1956 *et al.*).

Another approach to determine whether an external mass transfer resistance is present is to compare the observed reaction rate with the theoretically calculated rate of mass transfer (Levenspiel, 1999: p401). In this case the rate of external mass transfer is calculated in the extreme case where the surface reaction rate is assumed so fast compared to the mass transfer rate, that all reactants react as soon as they reach the catalyst surface. This means that the surface concentration of all reactants will be zero. In their studies on esterification catalysed by cation exchange resins, Yadav and Kulkarni (2000) and Yadav and Thathagar (2002) used this approach. They concluded that external mass transfer effects are negligible compared to the surface reaction and intraparticle diffusion based on the fact that:

$$\frac{1}{r_{\text{obs}}} \gg \frac{1}{k_{cA} C_{Ab}} \gg \frac{1}{k_{cB} C_{Bb}} \dots \dots \dots \quad (13)$$

Where k_c is the mass transfer coefficient of each reactant in m/s and C_{ib} refers to the bulk concentration of reactant A and B respectively. In this case the observed rate (r''_{obs}) is in terms of the external surface area of the catalyst in order to give consistent units. The ability to use this analysis depends on the availability of data or suitable correlations for the mass transfer coefficients for all the reactants.

2.2.3. Intraparticle diffusion

The stagnant fluid in catalyst pores presents a major diffusional resistance to transport between the ambient stream and the interior of the porous material. In many heterogeneous systems, internal mass transfer influences the overall reaction rate. This implies that a concentration gradient is established inside the catalyst bead and that interior surfaces are exposed to lower reactant concentrations. For isothermal reactions, the overall reaction rate is then usually less than when no diffusional effects influence the reaction. The apparent activation energy, reaction order as well as the catalyst selectivity is also dependant on this phenomenon (Satterfield, 1970: 129-130).

Internal effectiveness factor and the Thiele Modulus

The effect of the variations in concentration throughout the pellet on the reaction rate is quantified with a parameter referred to as the internal effectiveness factor (Fogler, 1999: 738). This internal effectiveness factor indicates the relative importance of diffusion and reaction limitations. It is defined as:

$$\eta = \frac{\text{actual measured overall rate of reaction}}{\text{rate of reaction if entire interior surface exposed to the external surface conditions } C_{As}, T_s}$$

The Thiele model is generally used in literature on catalytic reactions as a means of calculating this parameter in heterogeneous catalysis (Gates, 1992:225-228; Fogler, 1999: 742-746). In this theoretical approach, the equations for simultaneous mass transfer and chemical reaction are combined in a steady state mole balance over a catalyst particle.

Ficks law is used to describe the diffusional flux in a porous particle (Gates, 1992: 226):

$$J_{AB} = D_e \frac{dC_A}{dR} (14)$$

Where

J_A = Intraparticle diffusional flux in mol/m.s

D_e = Effective diffusivity of component A in the mixture, m²/s

C_A = Concentration of A, mol/m³

R = Resin particle radius, m

The effective diffusivity accounts for the resin porosity, tortuosity an varying cross-sectional areas of the resin pores (Fogler, 1999:739-740):

$$D_e = \frac{D_A \varepsilon_p \sigma}{\tau} \text{ m}^2/\text{s} (15)$$

Where

D_A = Molecular diffusion coefficient of component A in the mixture,

m^2/s

τ = Tortuosity

ε_p = Pellet porosity

σ =Constriction factor (accounting for the variation in the cross-sectional area that is normal to diffusion)

The simplest analytical treatment of the particle mole balance can be illustrated with an irreversible n^{th} order reaction where adsorption and desorption have no effect on the reaction rate. After introducing appropriate boundary conditions for concentration, the resulting differential equation can be solved in a dimensionless form.

The solution is a function of the parameter that is defined as the Thiele modulus $-\phi$, where:

$$\phi^2 = \frac{kC_{As}^n R}{D_e(C_{As} - 0)/R} = \frac{"a" \text{ reaction rate (based on catalyst volume)}}{"a" \text{ diffusion rate}} \dots \dots \dots (16)$$

So that for an irreversible first order reaction the dimensionless Thiele modulus is:

Where:

k	Rate constant	s^{-1}
R	Catalyst particle radius	m

When the Thiele modulus is large, internal diffusion usually limits the overall

rate of reaction. When the modulus is small, the surface reaction is the rate-limiting step.

The previously defined effectiveness factor can now be calculated in terms of the Thiele modulus. It can be shown that for a first order irreversible reaction the effectiveness factor can be calculated with:

There are two limiting cases for the use of this equation.

The first, if $\phi \ll 1$, then $\eta \approx 1$ and the rate = kC_{As} . From the definition of ϕ that is possible when:

- The particle radius R approaches zero
 - When D_e the diffusion coefficient of the reactant in the catalyst particle becomes very large
 - When the catalytic activity indicated by k becomes very small

The second limiting case is when ϕ becomes very large, then

$$\eta = \frac{3}{\phi}$$

and the reaction rate for a first order reaction becomes:

$$-r_A = \eta k C_{As} = 3k \frac{1}{R} \left(\frac{D}{k} \right)^{1/2} C_{As} \quad \dots \dots \dots \quad (19)$$

The Weisz criteria for intraparticle diffusion

In order to evaluate the Thiele modulus, values of the effective diffusivity, the intrinsic reaction rate constant and the pore lengths are needed. The intrinsic rate constant can only be obtained if internal diffusion has no effect on the reaction. Measured kinetics might incorporate internal diffusion effects – making it difficult to determine the intrinsic rate constant and therefore the

Thiele modulus. The Weisz modulus is introduced to overcome this problem (Levenspiel, 1999:388).

The Weisz-criterion (sometimes referred to as the Weisz-Prater criterion) uses measured reaction rates to determine whether internal diffusion is limiting the reaction. For a first order irreversible reaction:

The reaction rate (r') in this case is per unit mass (g) of catalyst and p_c is the catalyst density in g/m^3 . If $\Phi_{WP} \ll 1$ there are no diffusion limitations and consequently no concentration gradient exists within the pellet. If $\Phi_{WP} \gg 1$ internal diffusion limits the reaction severely (Fogler, 1999:758-759).

Satterfield (1970: 205-206) estimates that diffusion effects will definitely be present if $\Phi_{WP} \geq 6$ and that diffusion can be assumed to be insignificant when $\Phi_{WP} \leq 0.3$.

The above-mentioned model for describing internal diffusion effects is restricted to power law, irreversible reaction kinetics. However, kinetics encountered in reactions catalysed by ion-exchange resins are mostly more complex – representing competitive adsorption and saturation (Gates, 1992:228). In such complicated cases the effectiveness factor can still be given as a function of the Weisz modulus but the derivation of the η - Φ_{WP} relationship involves complex numerical calculations that includes several additional parameters (Gates, 1992: 232). Satterfield (1970:184-198) gives graphical representations of η - Φ_{WP} relationships for a variety of more complex reactions, specifically those cases where the reaction is reversible and follows Langmuir-Hinshelwood kinetics. In this case the effectiveness factor is a function not only of the Weisz modulus, but also of three additional parameters. These parameters are functions of the equilibrium concentrations, adsorption equilibrium constants for reactants and products as well as diffusivities - all parameters that may not be known for the system under investigation. The calculation of the effective diffusivity, especially in

liquid systems, also complicates the analysis.

In liquid systems there are considerable variation in the molecular diffusion coefficient, D_A , with concentration. In addition, little information is available on the effect of temperature on diffusion in the liquid phase. Satterfield (1970: 18) gives some of the more frequently used empirical correlations to use in order to estimate liquid diffusivities but mentions that errors when using such correlations are in the order of 10-15% for aqueous systems and considerably greater in the case of organic solvents.

Despite the above-mentioned difficulties in calculating the Weisz-modulus, many researchers on cation exchange resin catalysis use the criterion to establish whether they are in an internal diffusion limited regime (Yadav and Thathagar, 2002; Limbeck, Altwicker and Kunz, 2001; Yadav and Kulkarni, 2000). They all use a constant value for binary molecular diffusivity, and treat the reaction rate as first order and irreversible – irrespective of the final form of the rate expression that they develop.

An experimental approach to evaluate the importance of internal diffusion is to conduct experiments where the only changed variable is the catalyst particle diameter. If the rate proves to be independent of particle diameter, it is an indication that intraparticle diffusion is negligible (Helfferich, 1962: 547). This experimental approach is popular because no data on component diffusivities and resin tortuosity and porosity is required (Rihko-Stuckmann *et al.*, 2001; Schwarzer *et al.*, 2000; Saha, 1999; Kahn and Rahman, 1996; Klein and Banchero, 1956).

2.3. Effect of water on the reaction rate

Several authors acknowledged and investigated the detrimental effect of the presence of water on reaction rates of reactions catalysed by cation exchange resins (Limbeck *et al.*, 2001; Yang *et al.*, 2000; Kawase *et al.*, 1999 ; Chakrabarti and Sharma, 1993; Gates, 1992 : 187-195).

According to Chakrabarti and Sharma (1993), resin-catalysed reactions can be divided into two major types: Type A reactions, where water is part of the

initial reaction mixture, and type B, where no water is present initially. Type A reactions can be divided into aqueous reacting systems (A_1) or mixed organo/water (A_2) systems. In the case of type A_1 systems, the acid groups in the hydrated gel are completely dissociated as a result of the presence of the polar water molecules. Here the hydrated proton moves freely within the pore liquid and acts as the catalytic agent – similar to acid catalysis with a homogeneous acid. The pseudo-homogeneous approach is therefore applicable to these A_1 reaction systems. It is for this reason that reactions like the dehydration of t-butyl alcohol to give isobutylene in a strongly hydrated gel (high water concentration in the reaction mixture) shows nearly the same reaction rate as the same reaction in an aqueous solution of a strong acid.

In the case of A_2 reactions, water acts as an inhibiting factor and the catalyst is less effective than its homogeneous counterpart. Chakrabarti and Sharma (1993) base this fact on the observation that the cation exchange resin catalysed hydrolysis of a series of esters was more effective with pure water as solvent (A_1 system) than when 70% acetone was used as solvent. Here, the presence of acetone changes the distribution of the ester in favour of the bulk solution while the pores of the ion exchange resin are enriched by water. The lower concentration of ester inside the pores leads to a lower efficiency of the resin catalyst.

According to Chakrabarti and Sharma (1993), the non-aqueous type B reactions can also be subdivided into two groups: Systems where water is not one of the reaction products (B_1) and systems where water is one of the products (B_2). In type B systems, the acid groups might not be solvated so that the undissociated sulphonic acid groups on the polymeric matrix are the catalytically active groups. These are similar to systems described by the pseudo-heterogeneous reaction model. Any water present in these systems - either due to formation as a reaction product (B_2) or contamination of the reactants (B_1 and B_2) - has a high affinity for and bonds strongly with the sulphonic acid groups (Gates, 1992: 187-195). It therefore competes with the other reactants for the active sites. One water molecule attaches itself to four

sulphonic acid groups leading to a reduction in the number of available acid sites. Water therefore has a strong detrimental effect on B type reactions. In order for high catalytic activity to be maintained in B₂ type reactions, the water needs to be removed as soon as it is generated. Reaction rate data shows that when the water concentration is very low it inhibits the reaction whereas at high water concentration it simply dilutes the reactant as the reacting system changes from type B₂ to A₂.

Limbeck *et al.* (2001) observed this transition in their work on the synthesis of tetrahydrofuran (THF) by the splitting of water from butanediol (BD) over a cation exchange resin – a type B₂ reaction system. The presence of a small amount of water in the initial reaction mixture lead to a tremendous decrease of the reaction rate while the rate inhibiting effect was much less significant when large amounts of water were present at the beginning of the reaction (activity of water more than 0.75). Their experiments further showed that the addition of THF to the reaction mixture has nearly no effect on the rate.

A rate equation based on Michaelis-Menten kinetics (equation 21) accounted well for the initial reaction rates when no water was added to the mixture.

Where r_0 is the initial rate of the reaction related to the number of sulphonic acid groups, K_{sBD} the equilibrium adsorption constant of BD, k the rate constant of the reaction and a_{BD} the activity of BD.

However, as the reaction proceeded and more water was formed, the expression needed to be corrected for the inhibition effect of the water. They attempted to use Langmuir-Hinshelwood type kinetics to describe their experimental rate observations, but none of the mechanisms developed in such a manner proved to be successful. Even after using activities instead of concentrations in the rate expression they still had to incorporate an empirical “effectiveness factor” (equation 22) as a function of the activity of water to

quantify this effect:

Where K_{H_2O} is comparable to an adsorption constant for water. They too ascribe the rate inhibiting effect of water to the fact that water has such a high affinity for the $-SO_3H$ groups that it excludes the reactants from the catalytically active surface and suppresses the catalytic reaction almost completely.

Yang *et al* (2000) made the same observation when they investigated the possibility to synthesise ethyl-*tert*-butyl-ether (ETBE) from ethanol (EtOH) and *tert*-butyl alcohol (TBA) instead of the conventional EtOH/Isobutene route. In this case, other than in the conventional route, water is one of the reaction products (type B₂ reaction system)

The equilibrium reaction is then given as:



Their results also proved that the sulphonic acid groups of cation-exchange resins preferentially associates with the water in the reaction mixture and that the reaction rate is severely inhibited. In their attempt to quantify this effect, they included a temperature dependant inhibition coefficient for water in the reaction kinetics:

Where k_{10} and k_{10}' are the forward and reverse reaction rate constants respectively without the effect of water and K_w is the water inhibition coefficient. The rate could then be predicted with a power law rate expression

with the modified rate constants for the forward and the reverse reaction.

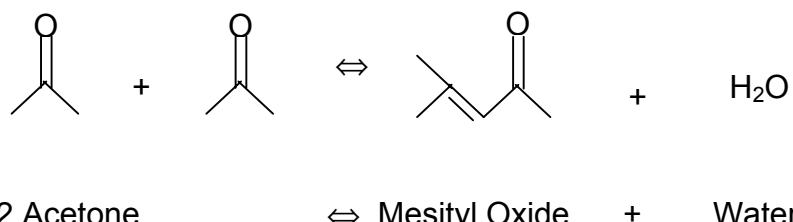
The reaction of acetone with phenol to produce bisphenol-A (an important chemical for producing a number of engineering resins) is another excellent example to illustrate the detrimental effect of water on the reaction rate (Kawase *et al*, 1999). Again, it was proven that the resin preferentially adsorbs water, the other reaction product, and that the catalytic activity is reduced. In order to simplify their batch reactor experiments, Kawase *et al* (1999) used an acetone to phenol ratio of 1:12. In this region, the reaction rate was first order with respect to acetone concentration in the initial period of the reaction. The activation energy from this initial data correlates well with other literature values for this reaction. After an acetone conversion of 50% was reached, the reaction rate decreased and the first order kinetics no longer described the behaviour of the reaction. Langmuir adsorption isotherms for all the reactants and products in the reaction were determined experimentally and confirmed preferential adsorption of water. After some simplifying assumptions the effect of water on the rate of disappearance of acetone was quantified by equation 25:

Where K_{H_2O} is the adsorption constant for water and C_{Ac}^* and $C_{H_2O}^*$ are the concentrations of the acetone and water when adsorption equilibrium is reached. Due to the fact that they only studied the reaction with excess phenol in the initial reaction mixture, it was not necessary to account for the reverse reaction. Whether this model would be applicable in a different concentration range, especially near reaction equilibrium, was not included in their investigation.

2.4. Reaction system studied

The reaction selected for this investigation was the condensation/dehydration of acetone to form mesityl oxide (MSO) and water on Amberlyst 16 ® - a commercially available cation exchange resin produced by Rohm and Haas.

The major reaction under consideration may then be represented as (Klein and Banchero, 1952):



2 Acetone \rightleftharpoons Mesityl Oxide + Water

Diacetone alcohol, the condensation reaction intermediate, is rapidly converted to MSO by the catalyst and no significant quantities were detected in the reaction mixture. This reaction fits the B₂ reaction system description where water is a reaction product and is expected to inhibit the rate of the resin catalysed reaction. In their work on the reaction kinetics of this system, Klein and Banchero (1956) proposed a rate expression but also mentioned that they were unable to model the reaction rate with their kinetic model if small amounts of water were added to the initial reaction mixture.

3. Experimental

3.1. Catalyst

Amberlyst 16 ® manufactured by Rohm and Haas was used as catalyst. It was used in the water-swollen state. The water content in the wet catalyst was incorporated into the mass balances and the kinetic expression. The intention was to develop an industrially applicable kinetic expression and therefore the catalyst was not grinded into smaller particles but was used as is. Some of the more relevant properties of the catalyst are given in Table 1 (Botes, 2003).

Table 1. Properties of Amberlyst 16 ®

Property	Value	Units
Minimum exchange capacity (dry basis)	4.8	eq/kg
Surface area	35	m ² /g
Particle size	0.6-0.8	mm
Density	780	g/l
Shape	beads	
Maximum operating temperature	120	°C

Analytical grade acetone supplied by Sigma Aldrich was used as reagent. It was not dried prior to use and the maximum water content of 0.02% was used in the mass balance.

3.2. Apparatus and Procedure

All experiments were carried out in a batch stainless steel reactor with reaction volume of 300 ml. Temperature control was achieved through heating elements fitted at three locations on the reactor wall. A thermocouple

in the reaction mixture and a thermocouple at the reactor wall were used to achieve accurate temperature control so that the reaction mixture isothermal at all time. The reactor was fitted with a mechanically driven agitator with variable speed control to ensure a homogeneous reaction mixture. Nitrogen pressure was applied to ensure that reactants and products remained in the liquid phase at all the temperatures investigated.

The desired amount of catalyst and the acetone was charged to the reactor before the heating process was initialised. The agitator was started only once the desired temperature was reached. This was then noted as the starting time of the reaction.

In some experiments, different amounts of MSO and water were added to the acetone before the mixture was charged to the reactor. This was necessary to quantify the effect of the reaction products, especially water, on the reaction rate. Initial MSO concentrations of 0.426 mol/l and 0.704 mol/l were used and in separate experiments initial water concentrations of 1.69 mol/l and 2.0 mol/l were investigated. Samples were taken through a needle valve. In order to maintain a relatively constant reaction volume in the reactor, each sample was limited to a volume of 1mℓ with an additional 1ml of mixture used to rinse the sample train. The sample was cooled through a coil immersed in ice water to prevent acetone evaporation during sampling. Figure 4 is a representation of the experimental set up.

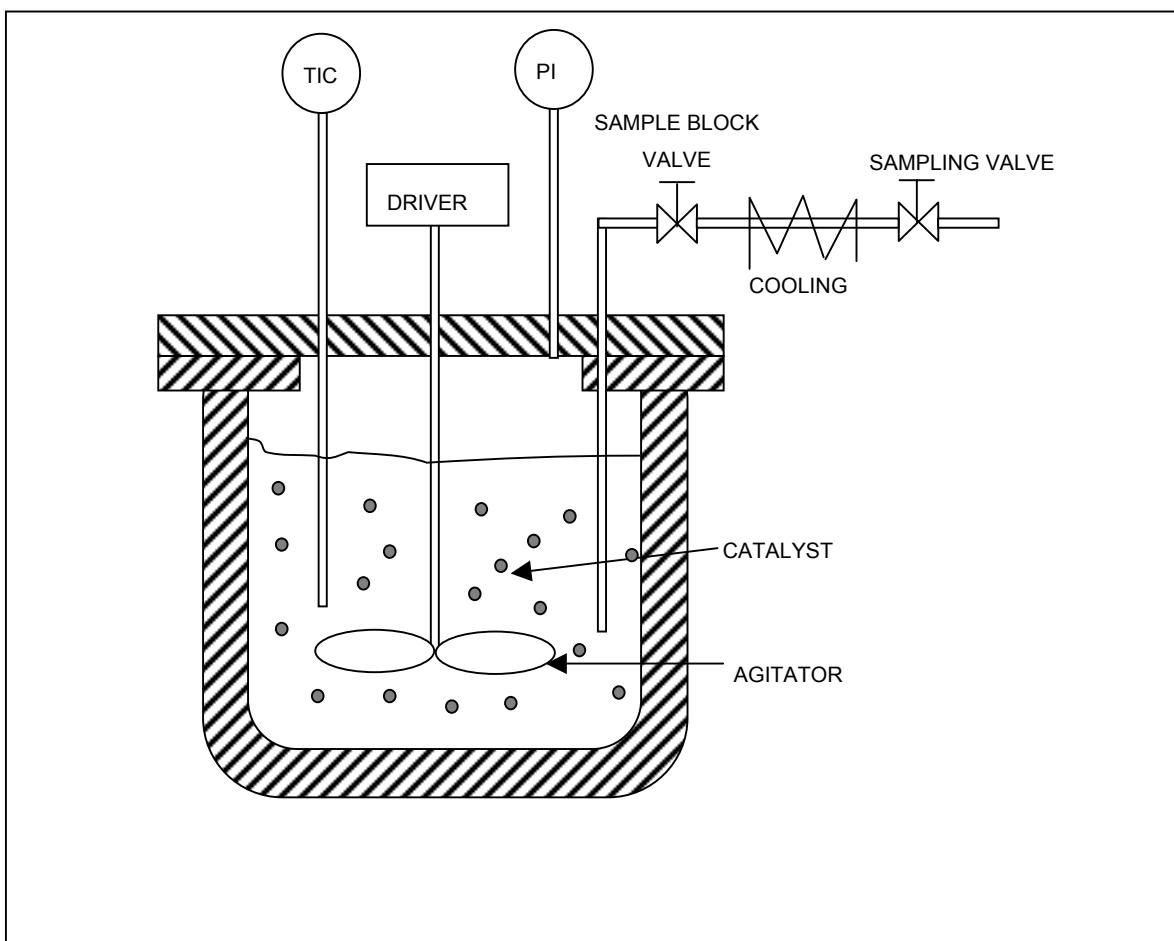


Figure 4: Experimental setup

3.3. Analysis

A Varian Star 3400 gas chromatograph (GC) was used to determine the amounts of acetone and MSO in the samples. The separation was carried out in a 30 m CP select 624 FS column with an inner diameter of 0.25 mm. Elution was established by Helium at a flow rate of 1 ml/min as the inert carrier gas with methyl isobutyl ketone (MIBK) as internal standard. The temperature profile for the column during one analysis was:

- 50-110°C with $\Delta T = 5^{\circ}\text{C}/\text{min}$
- 110-190°C with $\Delta T = 10^{\circ}\text{C}/\text{min}$

Total analysis time = 19 min

A flame ionisation detector (FID) was used. Due to the fact that a FID detects only carbon compounds, the water content, and as a result the concentration of all the components in the sample mixture, could not be determined directly with the GC. A mass balance that included the water content of the catalyst, the acetone and the water formed during the reaction was used to calculate the concentrations. The molar amount of water formed was assumed to be the same as that of the molar amount of MSO formed as the amount of higher condensation products were negligible compared to the amount of MSO. During their study of the same reaction system on a different catalyst, Klein and Banchero (1956) proved that this method is sufficiently accurate.

3.4. Repeatability

Experimental runs were repeated to determine the degree of experimental consistency. The absolute average percentage variation between repeat runs based on the MSO concentration was 8.8% when no reaction products were added to the reaction mixture and 8.9% when water or MSO was added to the reaction mixture. Figure 5a and 5b show the MSO concentration for sets of experiments with no water or MSO added and for experiments with MSO or water added to the initial reaction mixture. All the experimental data points generated were used to determine the kinetic model parameters and test the accuracy of the models in the subsequent sections.

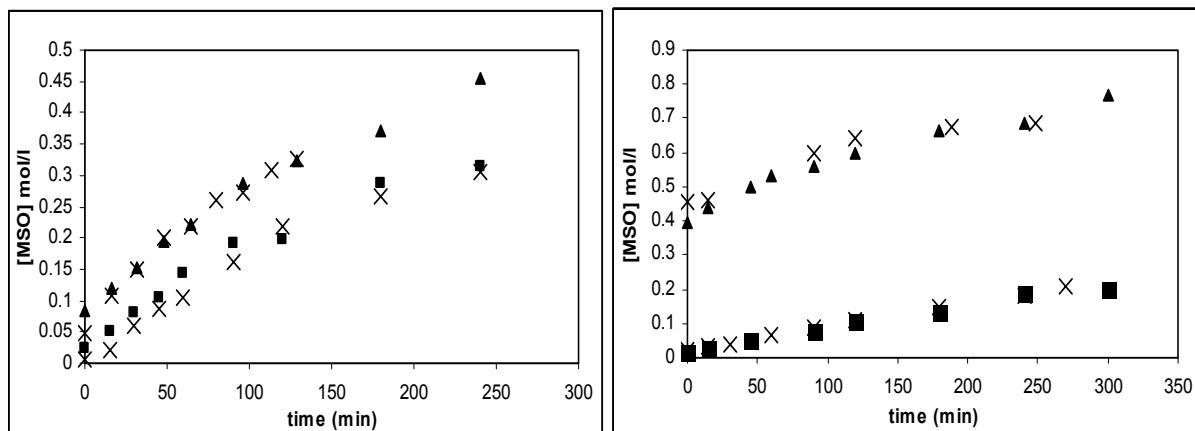


Figure 5a: Experimental repeatability with no products added to initial mixture. ▲ - 120°C, ■ - 105°C, x - repeat runs

Figure 5b: Experimental repeatability with water or MSO in initial mixture. ▲ - 0.426 mol/l MSO, ■ - 2.0 mol/l water, x - repeat runs

The repeatability of the analytical method was also confirmed. The maximum absolute percentage difference in the amount of MSO obtained between repeat analyses of the same sample for five samples in different concentration ranges was 1.37%.

3.5. External mass transfer

In order to study the intrinsic kinetics of the reaction it was important to ensure that the reaction rate was not limited by the rate of external mass transfer. The operating conditions that would satisfy this restriction were determined experimentally.

Vigorous agitation of the reaction mixture and a high liquid volume to catalyst mass ratio can achieve the elimination of external mass transfer limitations (Salmi, T et al., 2002). The liquid volume in this study was limited by the size of the reactor (300 ml). The maximum possible agitation rate of the mechanical agitator was 450 rpm. In order to determine the maximum amount of catalyst that could be used at this agitation rate without encountering external mass transfer effects, the initial reaction rate with different amounts of catalyst was compared at 120°C. This was expected to be the highest temperature investigated. The initial reaction rate would therefore be the fastest and the possibility that external mass transfer may be

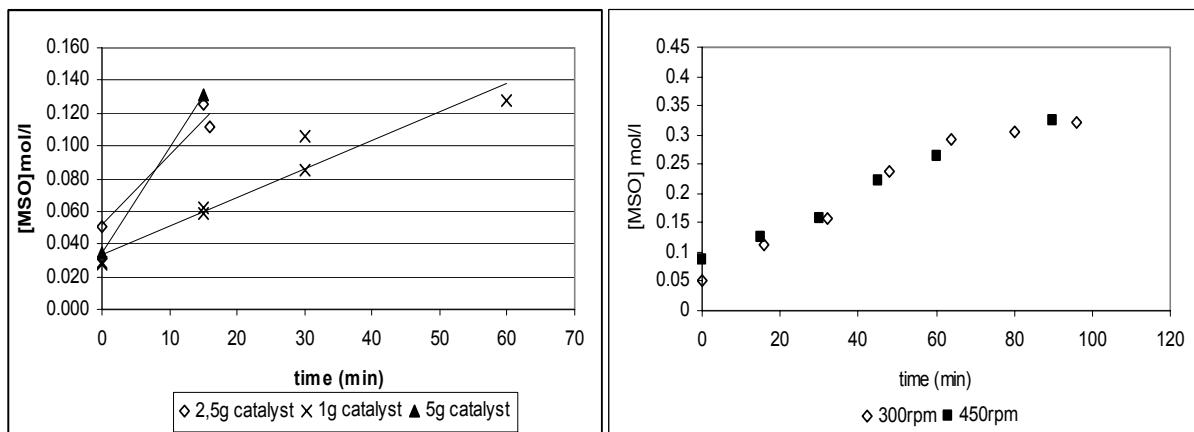


Figure 6. Initial change in MSO concentration with different amounts of catalyst

Figure 7. MSO concentration change at different agitation rates (2.5 g catalyst)

a limiting factor the greatest. (Experiments at 135° were eventually also conducted to increase the range in which the temperature dependence of the reaction rate was investigated, but external mass transfer was not reinvestigated at this temperature).

It was assumed that a direct relationship between the change in initial rate and an increase in catalyst weight is an indication that no mass transfer is present. The initial change in MSO concentration with time for the three different catalyst weights investigated (1g, 2.5g and 5g) is shown in Figure 6. The slope of a straight line through the data points between the 1 g and the 2.5 g catalyst experiments differs by a factor of approximately 2.5. However, the same relationship does not hold between the 2.5g and 5g catalyst experiments. A catalyst weight of 2.5g was subsequently used for all other experiments.

As final proof that no external mass transfer is present, the agitation rate was varied between two experiments conducted at otherwise identical operating conditions. The results (figure 7) showed no variation in initial reaction rate (measured as a change in MSO concentration with time) with a change in agitation speed. This indicated that external mass transfer does not influence the reaction rate. (Fogler, 1999: 706).

3.6. Intra-particle mass transfer

In order to determine whether intra-particle diffusion needed to be considered, a theoretical approach based on the Weisz-Prater modulus was followed. The diffusion of MSO out of the pores will be the only possible diffusion limitation of the reaction rate. As mentioned in section 2, the Weisz-Prater modulus can be seen as the ratio of “a reaction rate” to “a diffusion rate”. In this case, the rate of formation and diffusion of MSO was considered. The Weisz-Prater criterion in the form for power law irreversible reactions was used – even though the reaction is reversible and the rate expression of a complex nature. The assumption was that at initial conditions the reaction could be modelled as first order and irreversible. This is also the stage of the reaction where the diffusion rate of MSO would be the lowest and the reaction rate the highest – i.e. the worst-case scenario where Φ_{WP} will be the biggest. It was assumed that if $\Phi_{WP} < 0.3$ under these conditions, the possibility of diffusion as a rate controlling mechanism can be excluded. Equation 20 is repeated here for easy referencing:

The empirical Wilke-Chang correlation (Perry and Green, 1997: 5-50) was used to estimate the molecular diffusivity of MSO in acetone.

$$D_{MSO} = \frac{7.4 \times 10^{-8} (M_{Ac})^{1/2} T}{\mu_{Ac} V_{MSO}^{0.6}} \dots \quad (26)$$

Where:

M Molecular Weight (g/gmol)

V Molecular volume at normal boiling point (cm^3/gmol)

T Temperature (K)

μ Viscosity (cP)

The molecular diffusivity of MSO in acetone was calculated as 6.87×10^{-9} . m²/s. An effective diffusivity (Eq. 15) was calculated with estimated values for tortuosity and the constriction factor (Fogler, 1999: 741) and pellet porosity from the catalyst data sheet. Experimental values for the rate of MSO formation at 135°C were used. This was the highest temperature at which experiments were conducted; therefore the highest initial reaction rate. The value of the Weisz-Prater modulus obtained in this manner was 0.09. According to Levenspiel (1999:390) as well as Satterfield (1970: 205-206) this value indicates that diffusion can be neglected in the formulation of the rate expression. Even if a 20 % error were assumed for the Wilke-Chang correlation of diffusivity, the resultant value of $\Phi_{WP} = 0.11$ would still be below the suggested limits for diffusion control. All calculations are given in Appendix A.

3.7. Operating conditions

In their study of the same reaction system, Klein and Banchero (1956) were limited to a maximum temperature of 75°C due to catalyst deactivation. The temperature range investigated in this study was from 80°C to 135°. Even though the specified maximum operating temperature of the catalyst is 120°C, it has been successfully used industrially at temperatures of up to 130°C (Wasser, 2002). It was assumed that the catalyst would not deactivate at 135°C during the duration of one experimental run (approximately 4 h). Fresh catalyst was used for each run.

The vapour pressure of acetone – the most volatile component in the reaction mixture – at the maximum operating temperature is approximately 6 bar (ASPEN ® Properties). In order to prevent any evaporation, the reaction pressure was controlled at 10 bar.

4. Results and Discussion

4.1. Derivation of kinetic models

The two rate expressions derived in this work are based on the assumption that water blocks the catalytically active H⁺ ions from the reactant. This is similar to the B₂ type reaction systems described by Chakrabarti and Sharma (1993). It is therefore assumed that the reaction proceeds in a pseudo-heterogeneous manner and a simplified approach based on this fact is followed in the derivation of the models.

As mentioned by Kipling (1965:23) the term adsorption is used to describe the concentration of a particular component at an interface relative to an adjacent solution or other bulk phase. This definition is the one used to formulate the rate equations used in the analysis of the studied reaction system. The preference of the active sites on the catalyst surface for water, instead of the other components in the reaction system, is modelled as an adsorption process.

The effect of the concentration of the solute (in this case water) on the extent of adsorption at a certain temperature is mathematically described by an adsorption isotherm (Atkins, 1990: 885). For adsorption at the liquid-solid interface the isotherm is generally used to describe the amount of solute adsorbed from the liquid phase per unit mass of adsorbent. The most popular and oldest isotherm for adsorption of non-electrolytes from solution is the empirical Freundlich isotherm (Kipling, 1965: 24):

$$w = K_A C^{\frac{1}{\alpha}} \dots \quad (27)$$

Where w = mass or moles of solute absorbed per unit mass of adsorbent, K_A and α are constants and C is the equilibrium concentration of the component adsorbed in the bulk solution. The form $1/\alpha$ is specifically used to emphasise that C is raised to a power less than unity.

The Langmuir adsorption isotherm (equation 3) is mostly used for the

adsorption of gases on solids. The equation is repeated here for ease of referencing.

$$\theta_A = \frac{K_{S,A} C_A}{1 + K_{S,A} C_A} \dots \quad (3)$$

In this case θ is the fraction of adsorbent sites occupied by the gas. In some instances the Freundlich isotherm is also used to model the adsorption of gases on solid surfaces (Atkins, 1990: 886). Although the same form of the expression given in equation 27 is still used, in this case the model is used to quantify the fraction of adsorbent sites occupied by the gas instead of the amount of solute absorbed.

In the hypothesis proposed in this work, the adsorption isotherms are used to indicate the number of active sites on the catalyst blocked by water molecules – and therefore the actual number of sites available for participation in the reaction. The Langmuir adsorption isotherm is then used with

$$\theta = \frac{[\text{H}^+]_{\text{blocked by water}}}{[\text{H}^+]_{\text{TOTAL}}} \dots \quad (28)$$

In this work the Freundlich equation is used in a similar manner to give the extent of occupied sites as a function of the water concentration in the mixture, so that equation 27 can now be written as:

$$\theta = K_A C^{1/\alpha} \dots \quad (29)$$

It is common practice in cation resin catalysis to express the reaction rate in terms of the number of equivalent acid sites. Where water deactivates some of the acid sites, only the sites available to catalyse the reaction should be used in the rate expression. However, the rate equation expressed in terms of available number of sites can easily be related to a rate based on the total number of sites in the reaction system by using equation 30:

This would make the rate equation more convenient to use as the total

number of equivalents on a given weight of catalysts is a property of the specific catalyst and this information is available from the manufacturer of the catalyst. In this work it is assumed that the reaction in terms of the available number of acid sites can be described by a simple power law expression – even though it follows a pseudo-heterogeneous mechanism. The reaction rate in terms of the total number of acid sites will then be given by equation 31:

$$r = k_1 \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right) (1 - \theta) \dots \dots \dots (31)$$

Now r has units of mol/(eq.s) where the number of equivalents refer to the total added to the reaction system and not that available after site deactivation by water.

Depending on the type of adsorption isotherm used, different forms of the rate expression will result. If the Langmuir isotherm is assumed to describe the number of equivalents deactivated by water the rate expression becomes:

$$r = \frac{k_1 \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right)}{(1 + K_{SH2O})} \dots \dots \dots (32)$$

Where the Freundlich isotherm is used to describe the deactivation the expression becomes:

$$r = k_1 \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right) \left(1 - K_A [H_2O]^\alpha \right) \dots \dots \dots (33)$$

With K_{eq} the equilibrium constant for the reaction.

Both equation 32 and 33 were used to model the experimental results. In addition the applicability of the model proposed by Klein and Banchero (1956) were also reinvestigated:

$$r = \frac{k_1 \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right)}{(1 + K_{KB} [H_2O][MSO])} \dots \dots \dots (34)$$

The value for the equilibrium constant from their work was used in all the models:

$$K_{eq} = 6.20 \times 10^{-3} e^{\left(\frac{347}{T}\right)} \text{ with } T \text{ in K} \quad \dots \dots \dots \quad (35)$$

In each case the rate expression predicts the rate of formation of MSO per total number of equivalent acid sites.

4.2. Ability of proposed models to predict the reaction rate

4.2.1. Temperature dependent constants of each model

The experimental data that were generated at each of the five temperatures investigated with no MSO or water initially added to the reaction mixture were used to obtain the optimum temperature dependent parameter set for each model. All constants were solved by minimising the squared error between predicted and experimental values.

Klein & Banchero's model

Only the form of the rate equation proposed by Klein and Banchero (1956) was used. All the parameters were obtained by fitting the model to the experimental data in this study.

The rate constant, k_1 , follows an Arrhenius temperature dependence as depicted in figure 8. Although the constant below the line, K_{KB} , shows a linear dependence when $\ln K_{KB}$ is plotted against the inverse of temperature, (see figure 9) the slope of the line is opposite to what would be expected if K_{KB} was a reaction rate constant or an equilibrium adsorption constant. Klein & Banchero observed the same trend during their investigation and explained that this constant may be a ratio of rate constants resulting from a complicated rate mechanism. In theory the model therefore does not account for any

adsorption effects.

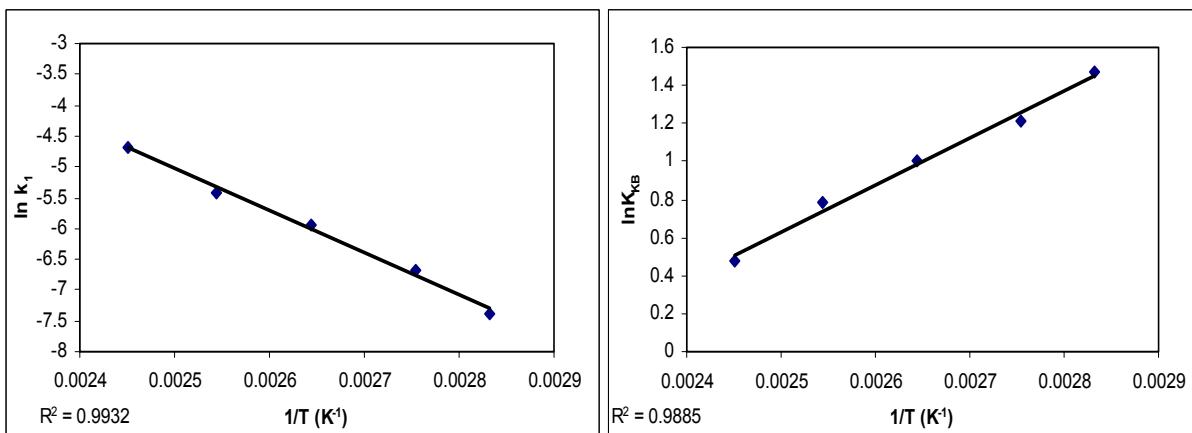


Figure 8: Temperature dependence of k_1 in Klein & Banchero's model

Figure 9: Temperature dependence of K_{KB} in Klein & Banchero's model

The final temperature dependant form of Klein and Banchero's model is given by equation 36:

$$r = \frac{64.6 \times 10^3 e^{-\frac{6531}{T}} \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right)}{\left(1 + 3.85 \times 10^{-3} e^{\frac{2476}{T}} [H_2O][MSO] \right)} \dots \dots \dots (36)$$

According to the temperature dependent rate constant, k_1 , the activation energy of the reaction is 54.3 kJ/mol, which is somewhat higher than the 41.1 kJ/mol calculated by Klein and Banchero.

The Langmuir model

Both constants in the Langmuir model, the rate constant k_1 and the adsorption equilibrium constant K_{sH_2O} , follow an Arrhenius temperature dependence indicating a negative enthalpy of adsorption. This is to be expected, as adsorption is generally exothermic (Atkins, 1990:885). Figure 10 and 11 graphically shows the relationship of the two constants with temperature.

The temperature dependant Langmuir model that gives the reaction rate based on the total number of equivalent sites is given by equation 37:

$$r = \frac{64.6 \times 10^3 e^{-\frac{6531}{T}} \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right)}{\left(1 + 85.0 e^{-\frac{2328}{T}} [H_2O] \right)} \dots \dots \dots (37)$$

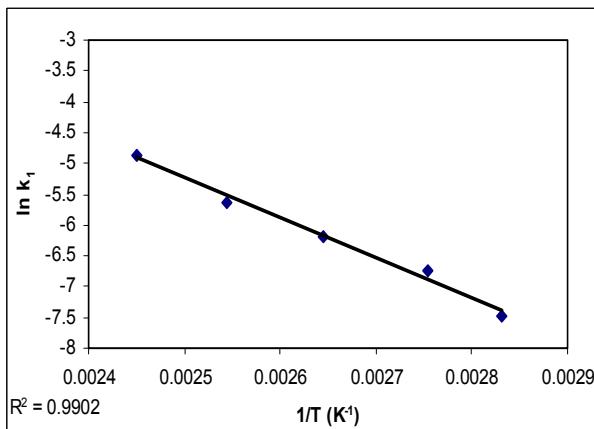


Figure 10: Temperature dependence of k_1 in the Langmuir model

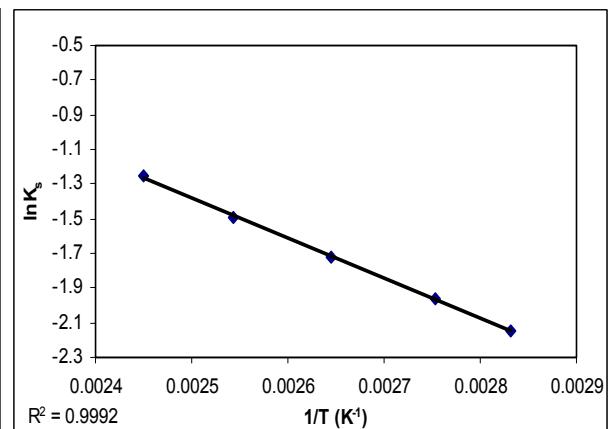


Figure 11: Temperature dependence of K_s in the Langmuir model

As with Klein and Banchero's model (solved with the current set of experimental data), the activation energy of the reaction was calculated as 54.3 kJ/mol.

The Freundlich model

When the Freundlich isotherm was initially used to describe adsorption from solution onto solid surfaces, it had no theoretical foundation and was purely empirical (Kipling, 1965: 25). Henry (1922) was the first to give a theoretical justification for its application to adsorption from solution. In his work he derives the Freundlich isotherm by combining an expression for the free energy of the surface with the Gibbs adsorption equation. The result shows that α must then be linearly dependant on $1/T$ while K_A is a constant independent of temperature.

The approach followed by Henry is only valid for dilute solutions of the component being adsorbed. Even though the water concentration range investigated in this study cannot necessarily be qualified as dilute (the

maximum mol percent water in the mixture was 17.5%), the same temperature dependence of the constants was assumed. Therefore, in addition to the minimisation of the square error, the constants were forced to adhere to these dependences when they were solved. With this approach the adsorption constant, K_A , has a value of 0.888 dmol and the temperature dependence obtained for α is shown in figure 12.

The rate constant, k_1 , still follows an Arrhenius temperature dependence as confirmed by the straight-line relationship obtained when $\ln k_1$ is plotted

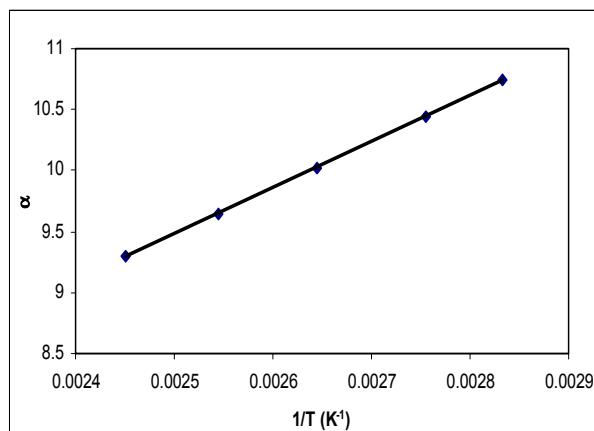


Figure 12: Temperature dependence of α in the Freundlich model

against $1/T$ in figure 13.

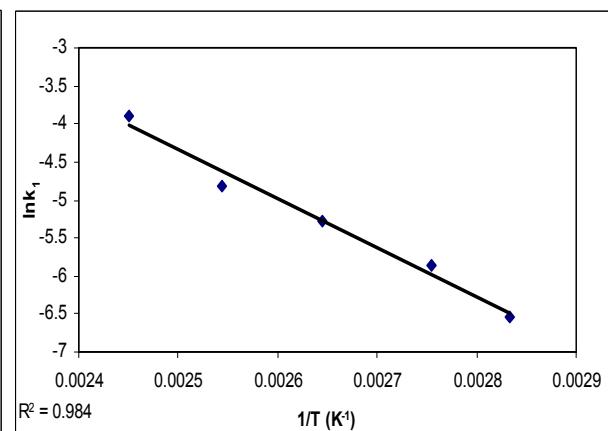


Figure 13: Temperature dependence of k_1 in the Freundlich model

The final form of the Freundlich model can now be given by equation 38:

$$r = 154.4 \times 10^3 e^{-\frac{6511}{T}} \left([Ac]^2 - \frac{1}{K_{eq}} [MSO] [H_2O] \right) \left(1 - 0.888 [H_2O]^{\frac{1}{3789}} \right) \dots \dots \dots (38)$$

Here the activation energy is calculated as 54.1 kJ/mol. The fact that the activation energy obtained with all the models is almost equal and constantly higher than that given by Klein and Banchero in 1956, indicates that their experimental conditions may not have been free from internal mass transfer effects.

4.2.2. Accuracy of models with no water or MSO in initial mixture

Figure 14a to 14c show the ability of the different models to predict the experimental results where no additional water or MSO were initially added to the reaction mixture. The results show that it is very difficult to distinguish between the different models in this concentration range. If the overall average error obtained with the different models are compared, it may seem as if the model proposed by Klein & Banchero still gives the most accurate prediction of the experimental results. However, not conclusively enough to suggest that it should be the model of choice. Average errors obtained with the different models are listed in table 2.

Table 2: Average error for models predicting experimental results with no water or MSO initially added to reaction mixture

Kinetic Model	Overall average error
Langmuir Isotherm Model	6.78%
Freundlich Isotherm Model	5.48%
Klein & Banchero Model	5.20%

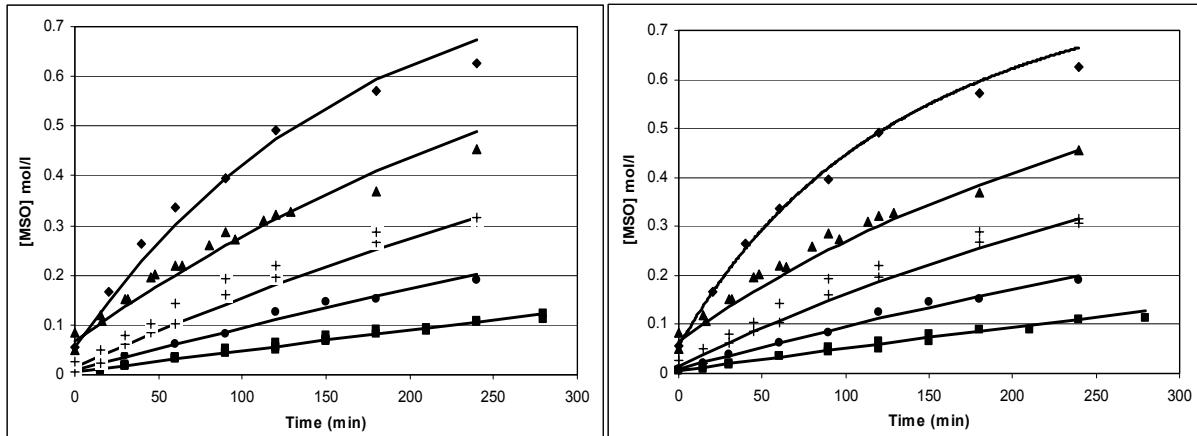


Figure 14a: The Langmuir model – no products added to reaction mixture.: \blacklozenge -135°C, \blacktriangle -120°C, $+$ -105°C, \bullet -90°C \blacksquare -80°C, — Model prediction

Figure 14b: The Freundlich model – no products added to reaction mixture.: \blacklozenge -135°C, \blacktriangle -120°C, $+$ -105°C, \bullet -90°C \blacksquare -80°C, — Model prediction

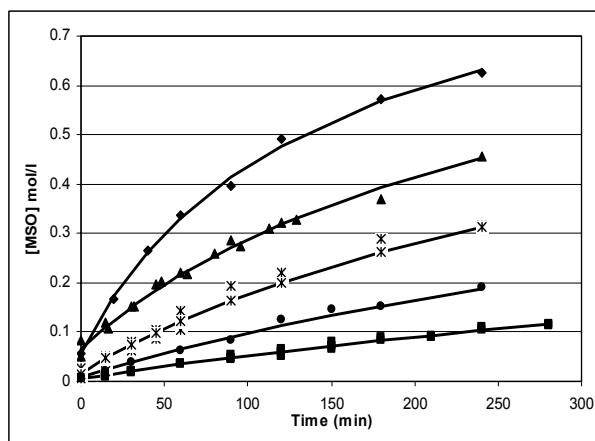


Figure 14c: Klein and Banchero model – no products added to reaction mixture.: \blacklozenge -135°C, \blacktriangle -120°C, $+$ -105°C, \bullet -90°C \blacksquare -80°C, — Model prediction

4.2.3. Performance of models with MSO added to the initial mixture

In this section the ability of each model to predict the formation rate when MSO was added to the initial reaction mixture was investigated. Here the aim was not to recalculate the constants for each kinetic model. Instead, the temperature dependant values for the constants obtained in section 4.2.1 were used to predict the reaction rate. (As it was not necessary to reinvestigate the temperature dependence of the models, all the experiments were conducted at 120°C).

The experimental results and model predictions with different amounts of

MSO added to the reaction mixture are shown in Figure 15a to 15c.

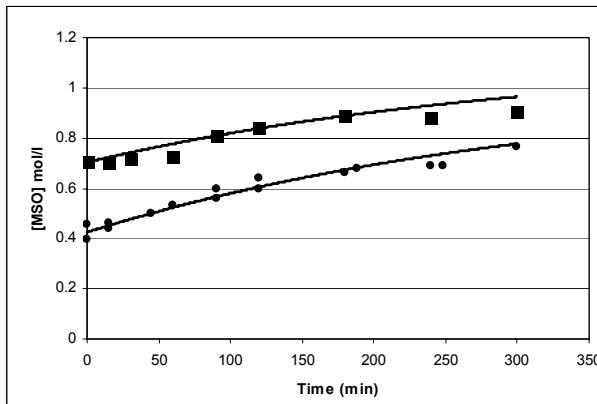


Figure 15a: Experimental data with MSO initially added: Prediction with the Langmuir model:
 • - $[MSO]_0 = 0.426 \text{ mol/l}$, ▀ - $[MSO]_0 = 0.704 \text{ mol/l}$,
 — Model prediction

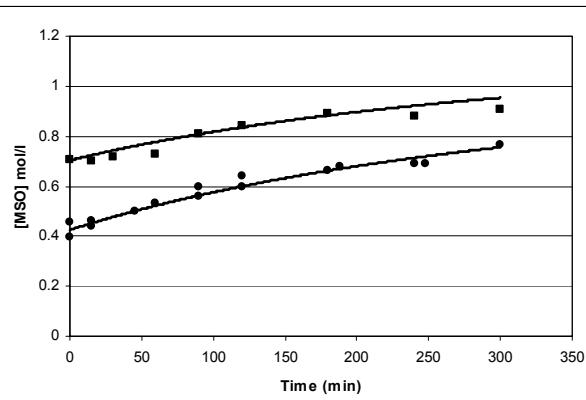


Figure 15b: Experimental data with MSO initially added: Prediction with the Freundlich model:
 • - $[MSO]_0 = 0.426 \text{ mol/l}$, ▀ - $[MSO]_0 = 0.704 \text{ mol/l}$,
 — Model prediction

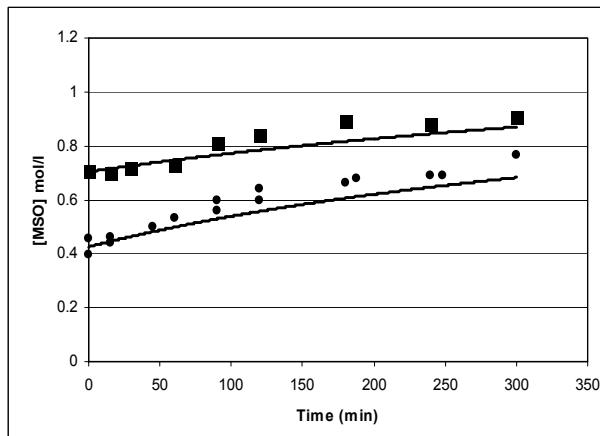


Figure 15c: Experimental data with MSO initially added: Prediction with Klein and Banchero model:
 • - $[MSO]_0 = 0.426 \text{ mol/l}$, ▀ - $[MSO]_0 = 0.704 \text{ mol/l}$,
 — Model prediction

The average error obtained with the model of Klein and Banchero is almost double that of the other two models (see table 3 for values). Their model constantly predicts an MSO concentration lower than that measured experimentally. This of course is a result of the appearance of the concentration of MSO in the denominator of the model. Although it may be an indication that the model is not suitable for this system, none of the errors obtained with any of the models is really significant. It can be concluded that all the models are still applicable in this concentration range.

Table 3: Average error between experimental data and model predictions with MSO initially added to the reaction mixture

Kinetic Model	Overall average error
Langmuir Isotherm Model	2.96%
Freundlich Isotherm Model	2.92%
Klein and Banchero Model	5.60%

4.2.4. Performance of models with water added to the initial mixture

The ability of the different models, with the same temperature dependant constants, to predict the rate of formation when water was initially added to the reaction mixture was also investigated. In this case the results showed a much more definitive distinction between the different models. Figure 16a to 16c gives a graphical representation of this fact.

It is clear that only the Freundlich model is able to predict the formation of MSO in this concentration range. Both the Langmuir- and Klein and Banchero's model underestimate the rate limiting effect of water. The average errors listed in table 4 emphasise this observation.

Table 4: Average error between experimental data and model predictions with MSO initially added to the reaction mixture

Kinetic Model	Overall average error
Langmuir Isotherm Model	54.58%
Freundlich Isotherm Model	6.54%
Klein and Banchero Model	71.05%

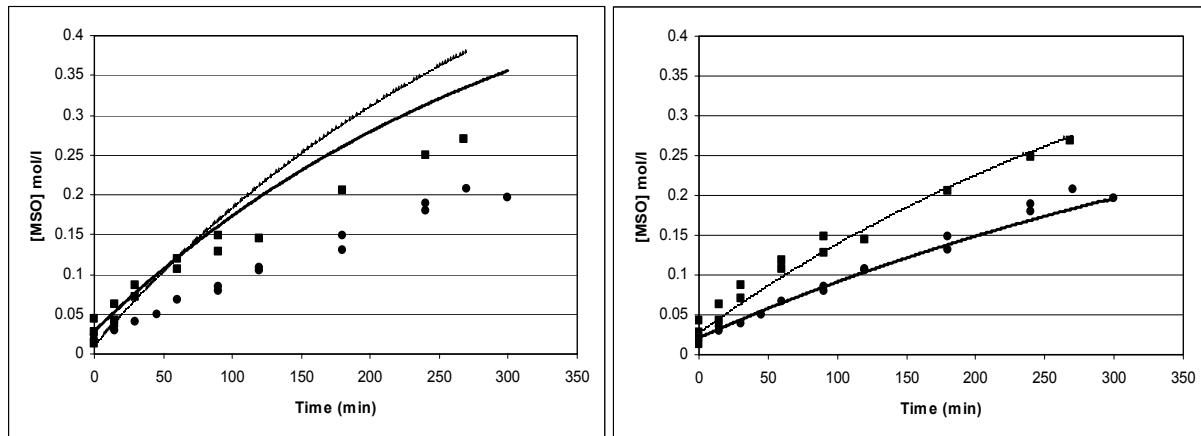


Figure 16a: Experimental data with H₂O initially added : Prediction with the Langmuir model:

• - [H₂O]₀ = 1.69 mol/l, ▀ - [H₂O]₀ = 2.0 mol/l,
— Model prediction

Figure 16b: Experimental data with H₂O initially added : Prediction with the Freundlich model:

• - [H₂O]₀ = 1.69 mol/l, ▀ - [H₂O]₀ = 2.0 mol/l,
— Model prediction

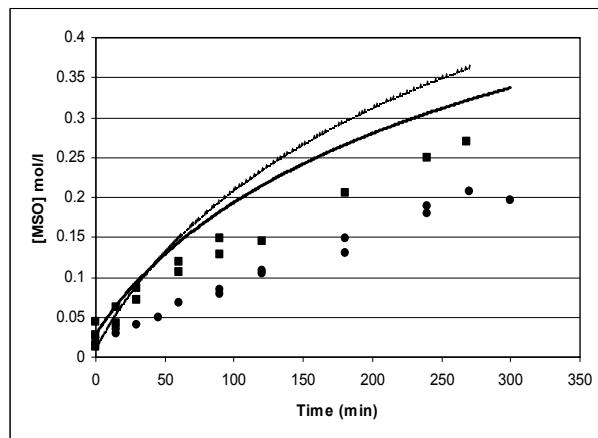


Figure 16c: Experimental data with H₂O initially added : Prediction with Klein and Banchero model

• - [H₂O]₀ = 1.69 mol/l, ▀ - [H₂O]₀ = 2.0 mol/l,
— Model prediction

This difference in performance by the models is significant enough to conclude that the Freundlich model is the only model suitable for this system over a wide concentration range.

4.3. Significance of the suitability of the Freundlich model

If the hypothesis that the adsorption isotherms can be used to determine the number of sites deactivated by the presence of water is true, then the fact that the Freundlich isotherm gives the best representation of the results is

understandable. In general this isotherm gives the best representation of adsorption phenomena in liquid solid-systems (Coulson and Richardson, 1991:766). The concept of monolayer coverage of the adsorbent, as assumed by the Langmuir isotherm is then also proven untrue for this system. Again this can be expected, as the blocking effect of the active sites cannot really be seen as adsorption on a solid surface. Instead, water molecules preferentially surround the $[H^+]$ ions.

All the proposed kinetic models have four parameters that needed to be solved to predict the temperature dependant reaction rate. It is worthwhile to note that no additional parameters needed to be incorporated into the Freundlich model in order to predict the experimental data over the whole concentration range – even when water was added to the initial reaction mixture. The same parameter set obtained when no products were added to the initial mixture (section 4.2.1) successfully predicted the formation rate of MSO for all other experimental conditions.

5. Conclusion

The study of the reaction where mesityl oxide and water are formed from acetone over a cation exchange resin catalyst confirmed the inhibiting effect of water as product on the rate of such reactions. Water associates preferentially with the catalytically active sites – effectively blocking them from the reactant. This effect can be modelled as if the water adsorbs on the catalytic sites. An adsorption isotherm can then be used to quantify the number of H^+ ions that are available to catalyse the reaction. This was combined with a simple power law expression to describe the rate per available acid site and incorporate the effect of the reverse reaction. The results showed that a Freundlich type adsorption isotherm gives a much more accurate prediction of this site deactivation effect of water than the Langmuir isotherm. Even when water was initially added to the reaction mixture the Freundlich model predicted the experimental results with an absolute average error of only 6.5% while the model based on a Langmuir adsorption isotherm gave an error of 54.6%. The model previously proposed for this reaction system by Klein and Banchero (1956) gave an error of 71.1% in this concentration range. It can therefore be concluded that the model based on a Freundlich adsorption isotherm for site deactivation was the only rate expression able to accurately predict the formation of MSO over a wide concentration range. The rate expression is given by:

$$r = 154.4 \times 10^3 e^{-\frac{651}{T}} \left([Ac]^2 - \frac{1}{K_{eq}} [MSO][H_2O] \right) \left(1 - 0.888 [H_2O]^{\frac{T}{3789}} \right)$$

Whether this approach is applicable to all similar reaction systems still remains to be investigated. However, it is recommended that it could be applied as a first option to other cation exchange resin catalysed reactions where water is one of the reaction products.

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APPENDIX A

Proving that internal mass transfer is negligible: Weisz-Prater Criteria

$$\Phi_{WP} = \frac{r_{MSO\ obs} \rho_c R^2}{D_e C_{MSO_s}}$$

For effective diffusivity (D_e):

$$D_e = \frac{D_{MSO} \phi_p \sigma}{\tau}$$

ϕ_p (pellet porosity)

0.4Amberlyst ® 16 Data Sheet

σ constriction factor

0.8(Fogler, 1999: 741)

τ tortuosity

3(Fogler, 1999: 741)

D_{MSO} : Molar diffusivity of MSO in Acetone: Estimated with Wilke-Chang correlation

$$D_{MSOAc} = 7.4 \times 10^{-8} \frac{(M_{Ac})^{1/2} T}{\mu_{Ac} V_{MSO}^{0.6}}$$

M Acetone 56g/mol

V_{MSO} 160.17581 cc/gmol

μ Acetone 0.1565cP

T = 408K

D_{MSO} = 6.87E-05cm²/s

D_e = 7.32E-06cm²/s 5.86E-06cm²/s (20%Error)

Rate: Initial rate of formation of MSO at 135°C (highest rate)

C_{MSO} @ t=0min	5.50E-05mol/cc
C_{MSO} @ t=20min	1.67E-04mol/cc
Catalyst mass	2.5g
Rate/g catalyst	3.73E-08mol/cc.s.g
Catalyst density ρ_c	0.78g/cc
Particle radius R	0.035cm

$\Phi_{WP} =$	0.09	with 20% error =	0.11
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