

## 4 Effect of Acid Strength on 1-Hexene Dimerisation

It is usually assumed for an acid-catalysed reaction that the rate of reaction is proportional to the acid strength of the catalyst. The literature review covering the effect of hydration on the oligomerisation of olefins summarises the importance of acid strength on the resulting products (Section 2.5). Investigations in the literature focused on the effect of acid strength on the oligomerisation of short chain olefins at a constant space velocity, but there is little in the literature to link the effect of acid strength to the reaction kinetics, especially when oligomerising/dimerising longer chain olefins.

Due to the hydrophilic nature of SPA, the addition of water to the reaction system would result in the adsorption of water to “*free acid*”, altering the acid strength of the catalyst and presumably resulting in an inhibited reaction rate. This allowed the opportunity of investigating the reaction rate at various acid strengths of the free acid by the addition of water or by the pre-treatment of the catalyst.

### 4.1 Experimental

To investigate the effect of the acid strength of SPA on the reaction rate of hexene dimerisation, batch experiments were completed at 150, 200 and 250 °C for various hydration levels within the catalyst. The acid strength of the catalyst was altered either by the addition of water or by the pre-treatment of the catalyst.

#### 4.1.1 Acid strength characterisation

The literature abounds with different methods to describe the acid strength of phosphoric acid, e.g. %  $H_3PO_4$  or %  $P_2O_5$ . For consistency, in this chapter the acid strength of the SPA is expressed as the fraction of phosphoric pentoxide ( $P_2O_5$ ) in water. Since the active phase of SPA is the supported liquid phosphoric acid (free acid), when the acid strength is discussed it is with reference to the strength of the free acid. Determining the activity of the catalyst requires that certain parameters of the catalyst should be known:

- Firstly, the free acid content. This is the weight fraction of free acid that is supported on the catalyst, expressed as weight percentage  $H_3PO_4$  per gram of catalyst.
- Secondly, the acid strength of the free acid. This is determined by the pre-treatment of the catalyst.

The acid strength of the phosphoric acid is fixed by the pre-treatment of the catalyst. Before any experiments were run as discussed in Chapter 3, the catalyst was first dried at 200 °C to ensure a constant hydration of the catalyst. This defines the base acid strength for this investigation; since the catalyst was left in the oven overnight it can be assumed that an equilibrium distribution of water and phosphoric acid is present for the acid. From the investigation of Ohtsuka & Aomura (1962) it was shown that heating of SPA at 200 °C stabilises at either 74.5%, 73% and 72% dependent on the type of kieselguhr support used for the preparation of the SPA. Since a Celite support, from America, was used for the SPA in this investigation the acid strength was taken as 72%. From Figure 2-5 it is evident that the acid distribution of the Celite SPA did not yet stabilise after 10 hours of pre-treatment at 200 °C. The difference between 72% (Celite) to 74.5% (Makkari kieselguhr, for which the acid distribution did stabilise) would however not influence the modelling of the reaction kinetics but only alter the base line acid strength. As such for all experiments completed in Chapter 3 the base line acid strength of the supported liquid phosphoric acid will be assumed to be 72% P<sub>2</sub>O<sub>5</sub> as well as further experimental work completed where the catalyst is pre-treated at 200 °C.

To determine the free acid content present on the dried catalyst, the technique described by Cavani *et al.* (1993) was used whereby the catalyst is washed with water at room temperature for 10 min – leaching off the supported liquid phosphoric acid. The acid concentration is then calculated from the quantity of acid neutralised by the titration of the leached acid with a 0.2 Molar solution NaOH to a pH of 4.62 (Coetzee *et al.*, 2006). The free acid content of the catalyst pre-treated at 200 °C was determined to be 21.6% (on a weight basis), which is similar to the values reported in the literature (Table 3-1).

This defined the free acid content of the catalyst as well as the acid strength of the SPA before the experiment started (as used in Chapter 3). Two sets of experiments were completed: firstly, to investigate the effect of free acid content at a constant temperature and secondly, to investigate the effect of the acid strength at various temperatures.

The effect of acid strength was investigated by altering the initial hydration of the catalyst. This was accomplished by the addition of water (up to 2000 ppm) to the solvent (and reagent) or by drying the tetradecane and solvent with a molecular sieve. The effect of hydrating/drying the catalyst at 150, 200 and 250 °C could then be determined with reference to the reaction kinetics of SPA baked at 200 °C (Chapter 3). Water was added to the solvent before the mixture was heated; meaning that once the reaction temperature was reached and the 1-hexene injected, the SPA had already adsorbed the added water and reached the desired

acid strength. The rest of the experimental procedure was kept similar as described in Section 3.2.2. For each experiment the P<sub>2</sub>O<sub>5</sub> percentage (acid strength) was subsequently calculated with reference to the base acid strength of 72% P<sub>2</sub>O<sub>5</sub> using Equation 4-1.

$$P_2O_5 (W\%) = \frac{P_2O_5^o * W_{Free\ acid}}{W_{Free\ acid} + W_{H_2O}} \quad 4-1$$

where W<sub>Free acid</sub> is the weight free acid content, as determined from the titration of the catalyst with NaOH, P<sub>2</sub>O<sub>5</sub><sup>o</sup> is defined as the base catalyst phosphoric acid strength and W<sub>H<sub>2</sub>O</sub> is defined as the quantity of grams of water added to the reaction mixture. The experiments that were completed to investigate the effect of hydration are shown in Table 4-1.

Table 4-1: Experiments completed where the catalyst was hydrated/dried at various temperatures.

T (°C)	State	m <sub>cat</sub> (g)	V (L)	Free acid content (W %)	Acid strength (% P <sub>2</sub> O <sub>5</sub> )
150	Hydrated	5.4	0.17	21.6%	60.5%
	Normal	7.2	0.18	21.6%	71.3%
		5.6	0.17	21.6%	71.3%
		21.4	0.15	21.6%	71.8%
200	Hydrated	5.0	0.20	21.6%	59.6%
	Normal	4.3	0.19	21.6%	70.8%
		5.1	0.21	21.6%	70.9%
		5.3	0.19	21.6%	71.0%
		15.1	0.18	21.6%	71.8%
	5.1	0.20	21.6%	71.5%	
250	Hydrated	5.8	0.29	21.6%	56.9%
	Normal	6.4	0.25	21.6%	70.9%
		8.0	0.25	21.6%	71.1%
		15.3	0.22	21.6%	71.8%

The effect of altering the free acid content was investigated on the reaction rate at 200 °C. The free acid content of the catalyst was manipulated by pre-treating the catalyst in one of two ways: 1) the catalyst was washed for 10 min in water and then dried at 200 °C; 2) the

catalyst was baked overnight in an oven at 600 °C (in an attempt to remove most of the free acid from the catalyst (Cavani *et al.*, 1993)). A reference point is needed to correlate the acid strength at this increased pre-treatment temperature. Since the acid strength for pre-treatment at 200 °C was close equilibrated value for acid strength, therefore the acid strength value was chosen as 86% P<sub>2</sub>O<sub>5</sub> (Brown and Whitt, 1952).

The methods described above can be used to give a complete overview of acid strength on the rate of 1-hexene dimerisation over SPA. Accordingly, to formulate the effect of acid strength and free acid content on the reaction rate, the experiments completed at 200 °C (shown in Table 4-1) could then be supplemented by the experiments where the free acid content was altered at 200 °C (listed in Table 4-2) to give an indication of the effect of free acid and acid strength on the reaction rates.

Table 4-2: Experiments completed to investigate the effect of acid strength on the reaction rate at 200 °C by altering the free acid content.

T (°C)	State	m <sub>cat</sub> (g)	V (L)	Free acid content (W %)	Acid strength (% P <sub>2</sub> O <sub>5</sub> )
200	<i>Baked 600 °C</i>	5.5	0.20	0.4%	49.8%
	<i>SPA washed and dried</i>	6.3	0.20	5.7%	66.4%
	<i>SPA washed and dried</i>	3.3	0.20	5.7%	66.4%

Two experiments were also completed with homogeneous ortho phosphoric acid (Sigma-Aldrich, 345245, ortho phosphoric acid 99.999%) and pyro phosphoric acid (Sigma-Aldrich, 43314, ≤ 80% pyro phosphoric acid) to gain an idea of the difference in the reactivity of the two acids. The experiments were completed by using a glass insert to protect the stainless steel reactor from the liquid phosphoric acid.

## 4.2 Results and discussion

The reaction kinetics was modelled as described in Section 3.4 for the experiments completed that were dependent on acid strength. The reaction rate was modelled by using an elementary kinetic model, shown in Equation 3-2 to 3-4 The AARE was minimised by optimising the rate constant applicable to a specific acid strength and temperature.

$$\frac{dC_A}{dt} = m_{cat}(-k_1C_A - k_3C_A C_B) \quad 3-2$$

$$\frac{dC_B}{dt} = m_{cat}\left(k_1C_A - k_2C_B^2 + \frac{k_2}{K_{eq}}C_D - k_3C_A C_B\right) \quad 3-3$$

$$\frac{dC_D}{dt} = m_{cat}\left(k_2C_B^2 - \frac{k_2}{K_{eq}}C_D + k_3C_A C_B\right) \quad 3-4$$

#### 4.2.1 Reaction rate for liquid ortho and pyro phosphoric acid

It has been shown that the acid strength of liquid phosphoric acid affects the rate of oligomerisation of short chain olefins (Bethea & Karchmer, 1956), Section 2.5. By contrast, this investigation was for liquid phosphoric acid with reference to propene, where no isomerisation can occur. To gain a preliminary idea of how the reaction rate of 1-hexene dimerisation changes, depending on the acid strength, 1-hexene was dimerised at 200 °C using both ortho and pyro phosphoric acid. Ortho phosphoric acid dehydrates to form pyro phosphoric acid (Equation 2-6):



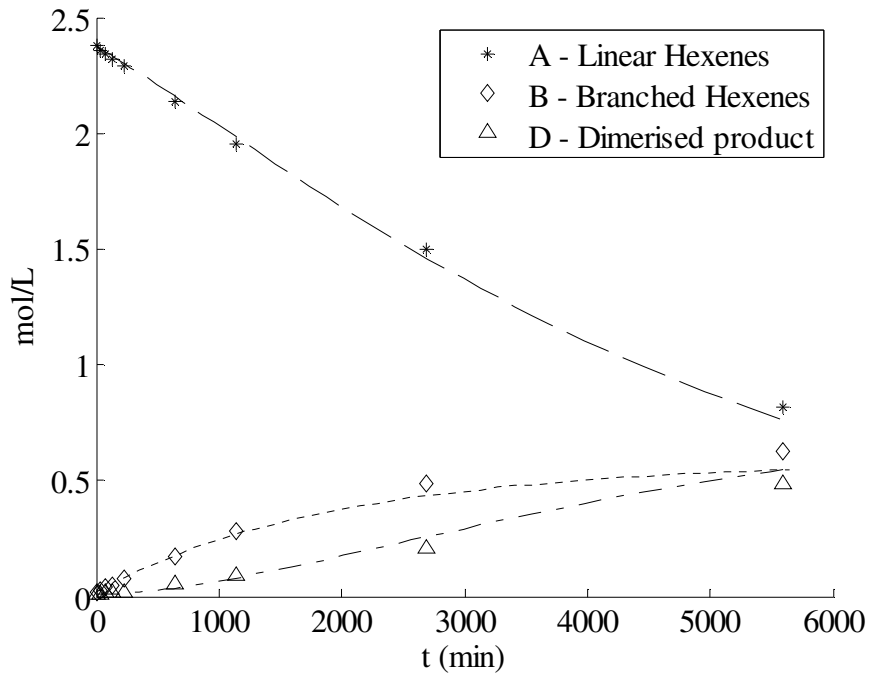
From the phosphoric acid distribution (ortho, pyro, tri phosphoric acid, etc.) measured by Jameson (1959) for various acid strengths of phosphoric acid (Figure 2-2), both ortho and pyro phosphoric acid will be present on the free acid on SPA. For low acid strengths (<68% P<sub>2</sub>O<sub>5</sub>), only ortho phosphoric acid should be present, whereas pyro phosphoric acid peaks at about 78% P<sub>2</sub>O<sub>5</sub>. One easy measure of the activity of the two acids is the dissociation constant of the acids (Section 2.4): the first dissociation constant for ortho phosphoric acid is 7.5×10<sup>-3</sup> whereas pyro phosphoric acid has a first dissociation constant of 1.4×10<sup>-1</sup>, indicating that pyro phosphoric acid is a much stronger acid. For this reason, the difference in the kinetics seen for ortho and pyro phosphoric acid is crucial to understanding how the reaction rate is affected by acid strength.

The kinetic parameters obtained from the optimisation are shown in Table 4-3, with the resulting description of the kinetic data shown in Figure 4-1 a) and b). Even though the kinetic parameters shown in Table 4-3 are based on the mass of the acid added, the comparison by mass will give a good indication of the difference in reactivity between the two acids due to dissociation. It is evident from Table 4-3 that pyro phosphoric acid is far more active toward the dimerisation of 1-hexenes. It can also be seen when comparing Figure 4-1 a) and b) that skeletal isomers form faster when pyro phosphoric acid is the catalyst (which is supported by the kinetic parameters).

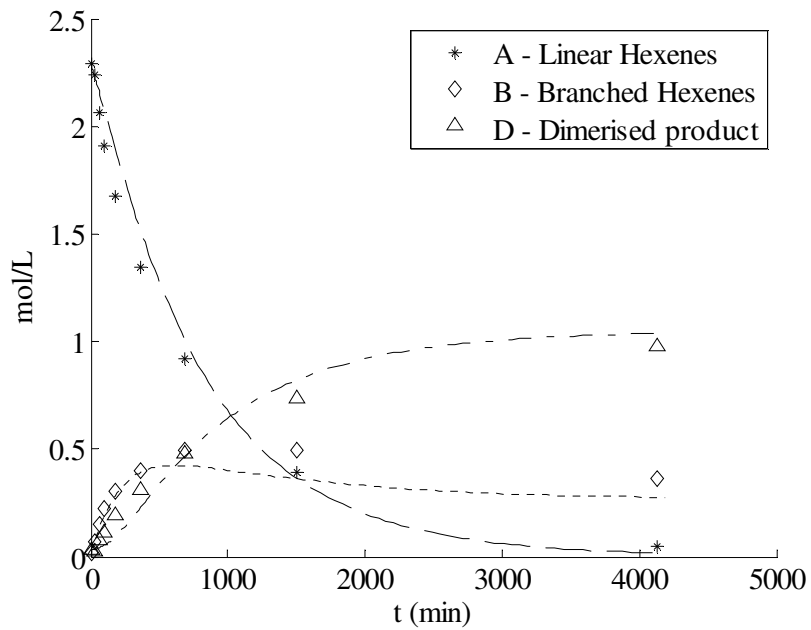
The increased in reaction rate with the increase in acid strength is to be expected. It is though intriguing that skeletal isomerisation and the dimerisation of branched hexenes (DBH) is affected to a much more significant extent than the rate of co-dimerisation (CD) of linear and branched hexenes. The change is due to skeletal isomerisation occurring more readily which results that CD occurs to a much lesser extent.

Table 4-3: Kinetic parameters obtained for the dimerisation of 1-hexene over liquid ortho and pyro phosphoric acid. Where the rate constants are for the various steps given in Figure 3-14, namely  $k_1$  – skeletal isomerisation,  $k_2$  – dimerisation of branched hexenes (DBH) and  $k_3$  – the co-dimerisation of linear and branched hexenes (CD).

	Pyro phosphoric acid	Ortho phosphoric acid
$k_1$ (L/min.g)	$30.6 \times 10^{-6}$	$4.1 \times 10^{-6}$
$k_2$ (L <sup>2</sup> /mol.min.g)	$107.6 \times 10^{-6}$	$27.6 \times 10^{-15}$
$k_3$ (L <sup>2</sup> /mol.min.g)	$27.0 \times 10^{-6}$	$7.9 \times 10^{-6}$



a) Ortho phosphoric acid



b) Pyro phosphoric acid

Figure 4-1: Dimerisation of 1-hexene at 200 °C over a) ortho phosphoric acid and b) pyro phosphoric acid where \* - linear hexenes, ◇ - branched hexenes and △ - total hexene depletion.

#### 4.2.2 Reaction kinetics for various acid strengths of SPA

Since the active phase for SPA is the free layer of phosphoric acid, the difference in reactivity between ortho and pyro phosphoric acid indicates that the activity of SPA should depend on the acid strength of the catalyst, especially taking into account that the variation in the acid strength will shift the free acid from completely ortho phosphoric acid to a mixture of ortho and pyro phosphoric acid (Figure 2-2). To estimate the effect of the acid strength of SPA, the rate of 1-hexene dimerisation was measured at a constant temperature (200 °C) for various acid strengths and acid loadings by pre-treating the reaction mixture and the catalyst. The resulting acid strength was expressed using Equation 4-1. The kinetic model expressed in Equation 3-3 to 3-4 was fitted to each individual experiment. The resulting prediction of the data is shown on each figure, Figure 4-2 and Figure 4-3. The end goal of the optimisation is to investigate the effect of acid strength on the rate constants.



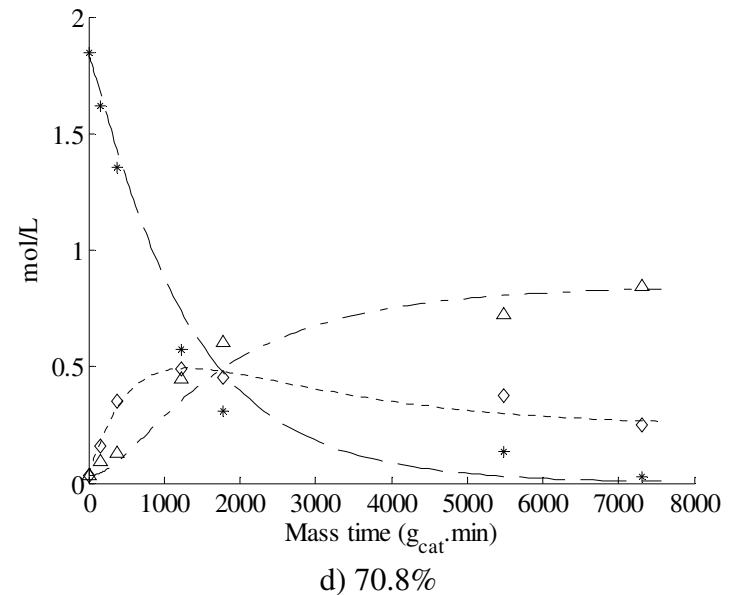
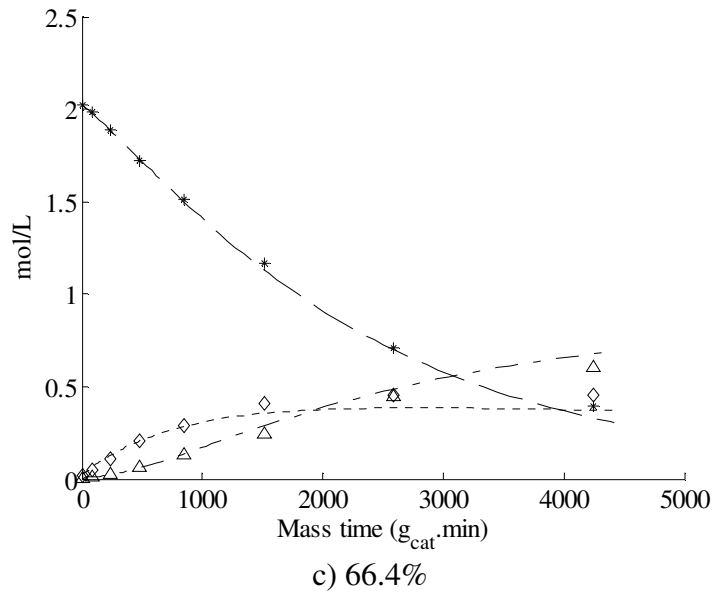
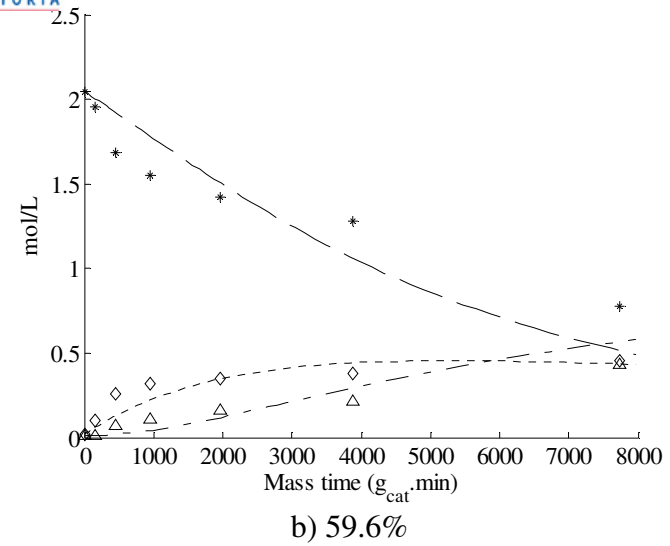
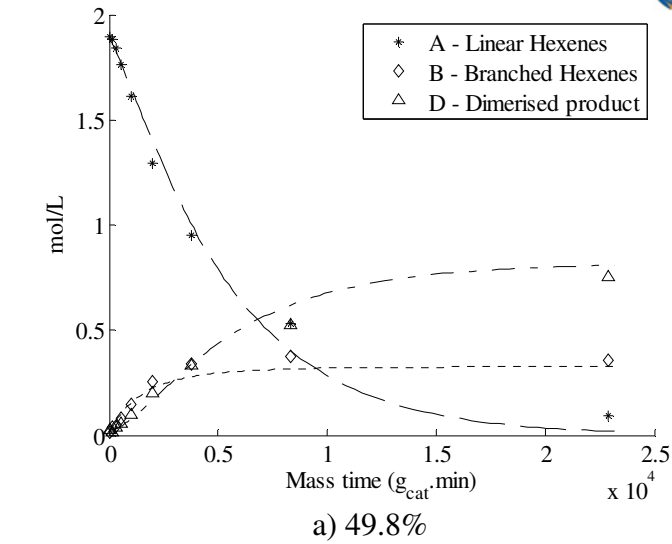


Figure 4-2: Reaction progression for the dimerisation of 1-hexene at 200 °C for acid strengths of 49.8% - 70.8% P<sub>2</sub>O<sub>5</sub> , with \* - linear hexenes,  $\diamond$  - branched hexenes and  $\triangle$  - total hexene depletion.

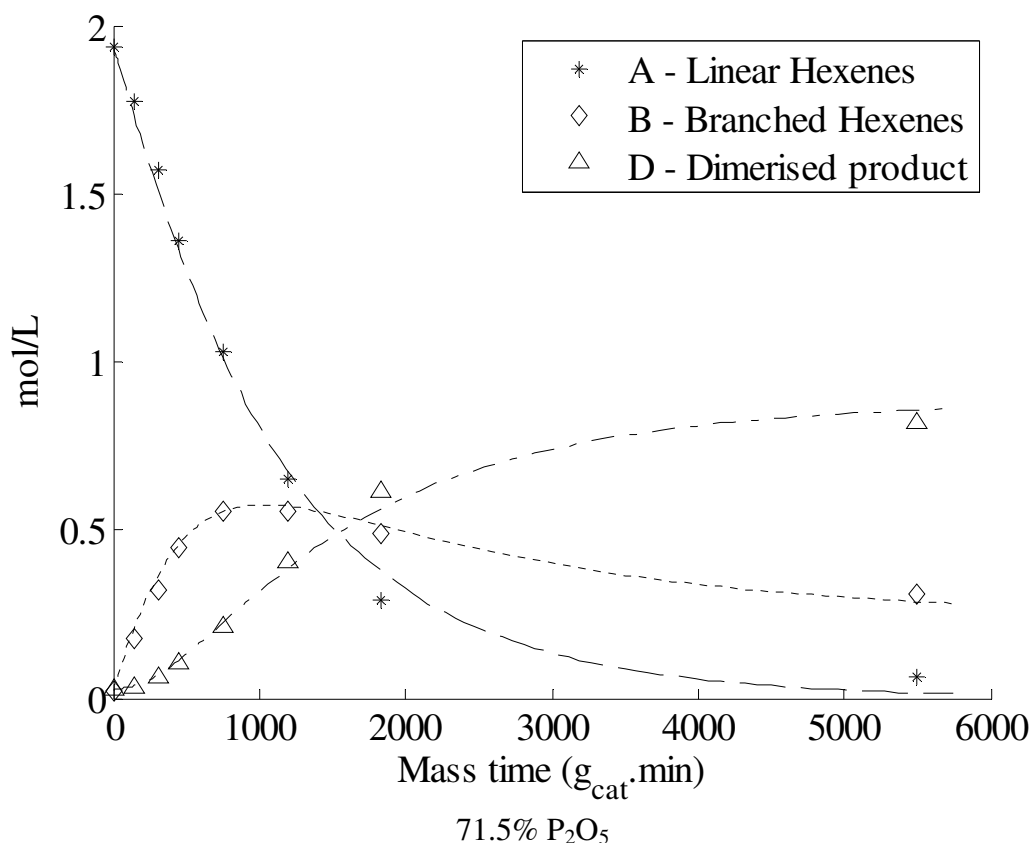


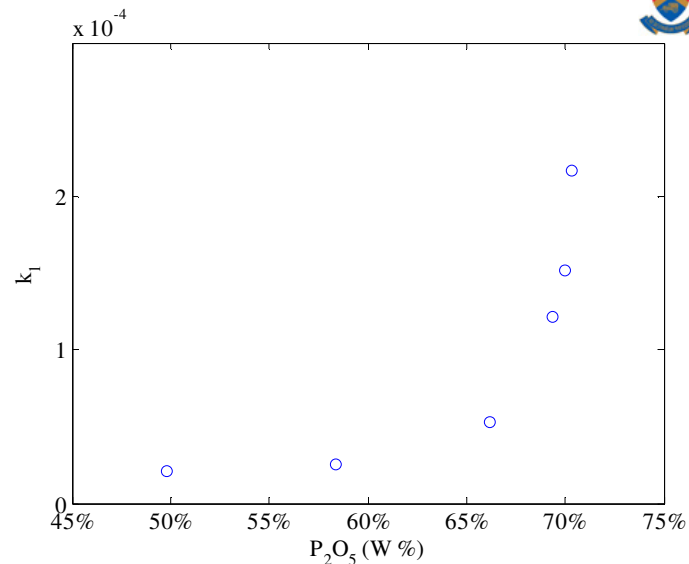
Figure 4-3: Reaction progression for the dimerisation of 1-hexene at 200 °C for an acid strength of 70.3% P<sub>2</sub>O<sub>5</sub>, with \* - linear hexenes,  $\diamond$  - branched hexenes and  $\triangle$  - total hexene depletion.

For the case where the catalyst was baked at 600 °C, Figure 4-2 a), there was still some catalytic activity. It could be plausible that the activity is due to silicon phosphates and the presence of trace amounts of water in the feed (<50 ppm water in the reaction mixture). It is not possible to eliminate the non-reactivity of the silicon phosphates. However, if the catalytic activity is attributed to the residual acid strength present in the catalyst (either due to un-evaporated phosphoric acid or due to hydration of silicon phosphates to free acid), the acid strength of the reaction would be 49.8%. The reaction rate of the dried catalyst is though nearly negligible in comparison to the normal untreated catalyst.

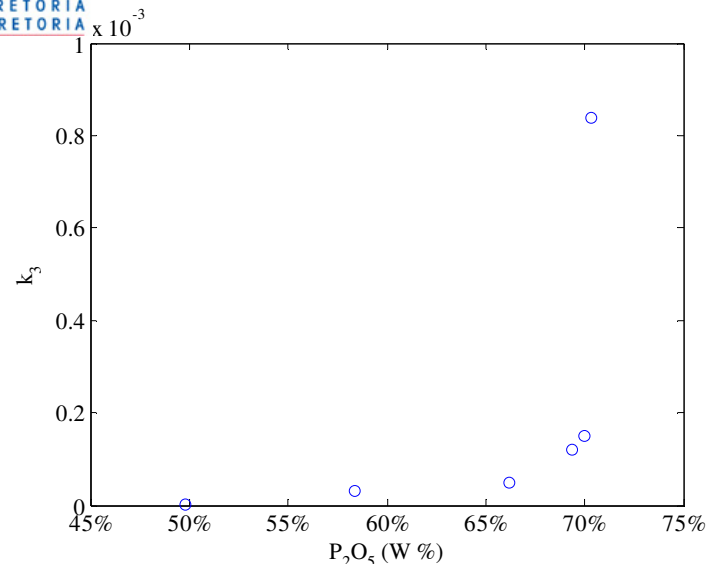
When looking at Figure 4-2 a) – d) and Figure 4-3, the effect of acid strength is noticeable on the rate of 1-hexene dimerisation. The total rate of hexene depletion increases from an acid strength of 49.8% P<sub>2</sub>O<sub>5</sub> to 71.5% P<sub>2</sub>O<sub>5</sub>. The reaction rate is therefore dependent on the acid strength. It is also evident that with an increase in the acid strength the formation of branched hexenes is also more significant. This suggests an increased propensity toward

skeletal isomerisation at higher acid strengths, which is beneficial for the total rate of hexene depletion. This corresponds to what was seen previously for ortho and pyro phosphoric acid (Table 4-3) and the findings of De Klerk (2004) for the oligomerisation of butenes over SPA. A more detailed analysis of the reaction rate is needed to distinguish how each reaction step is influenced by acid strength.

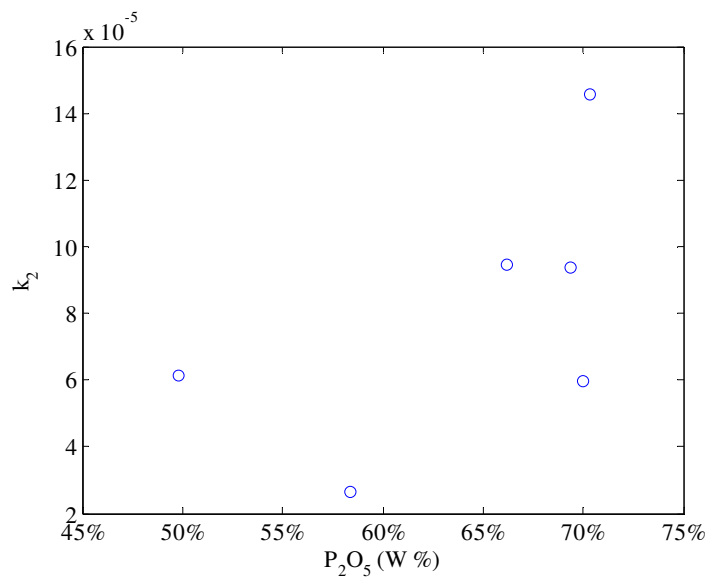
The resultant rate constants versus the acid strength of the catalyst are shown in Figure 4-4. An exponential growth is observed in the rate of constants for the formation of skeletal hexene isomers ( $k_1$ , Figure 4-4 *a*)) and the subsequent rate of dimerisation of branched hexenes (DBH) ( $k_2$ , Figure 4-4 *c*)). This corresponds to the increase in the first order rate constant predicted by Bethea & Karchmer (1956) for the oligomerisation of short chain olefins.



a)  $k_1$  Skeletal isomerisation (L/min.g)



c)  $k_2$  BHD ( $L^2/mol.min.g$ )



b)  $k_3$  CD ( $L^2/mol.min.g$ )

Figure 4-4: Rate constants versus acid strength on the rate constants at 200 °C,  $k_1$  – skeletal isomerisation,  $k_2$  – DBH and  $k_3$  – CD.

At low acid strengths the rate of co-dimerisation of linear and branched hexenes (CD) ( $k_3$ , Figure 4-4 b)) is similar to the rate of DBH ( $k_2$ , Figure 4-4 b)). As the acid strength increases the rate of isomerisation of branched hexenes increases significantly, which promotes the rate of DBH until the rate of CD becomes insignificant. This complicates the modelling of the rate of CD. Since the other rate constants are affected to an exponential extent by acid strength, it is plausible that the same trend would suffice for the rate of CD.

It can be seen from the dependence of the rate on acid strength for the rate of skeletal isomerisation ( $k_1$ ) and DBH ( $k_2$ ) that the reaction rate escalates suddenly at an acid strength of 68%  $P_2O_5$ . This is the phosphoric acid strength where the acid distribution shifts from predominantly ortho phosphoric acid to pyro phosphoric acid (Figure 2-2), indicating that pyro phosphoric acid is more active toward the dimerisation of hexenes. This corroborates the conclusion of Zhirong *et al.* (2000) that pyro phosphoric acid affects activity toward oligomerisation.

Experiments were also completed at 150, 200 and 250 °C for acid strengths of 60%, 70.5% and 71.8%  $P_2O_5$  respectively. The reaction rate was evaluated for each individual experiment, the experimental data and the resulting fits are shown in Figure 4-5 and Figure 4-6. The dependency of each rate constant on temperature, for a specific acid strength, can then be evaluated using the Arrhenius relationship, shown in Figure 4-7.

A negative activation energy is seen for the dimerisation of branched hexenes (Figure 4-7 c)), because the rate of BHD is dominated by CD at lower temperatures (150 °C). The exponential relationship with acid strength is clear, however, for the rate of skeletal isomerisation (Figure 4-7 a)) and the CD (Figure 4-7 b)). Typically the reaction rate increases with an increase in the acid strength of the catalyst. This is contrary to the finding by McClean (1987) that there is an inverse dependency of some rate constants with acid strength.

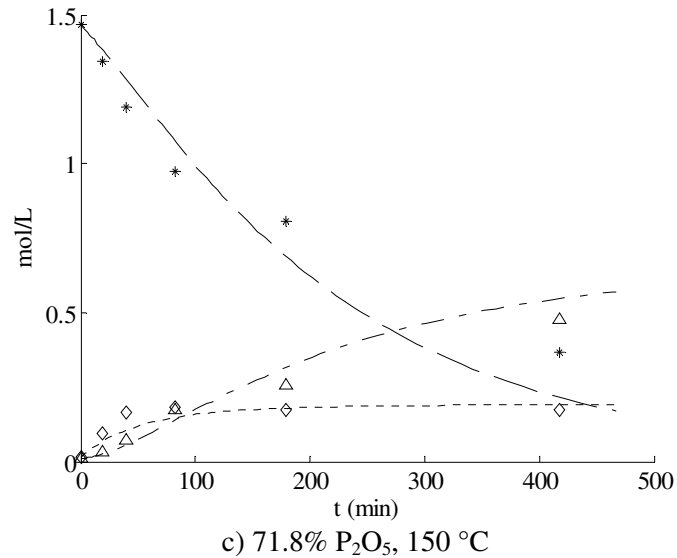
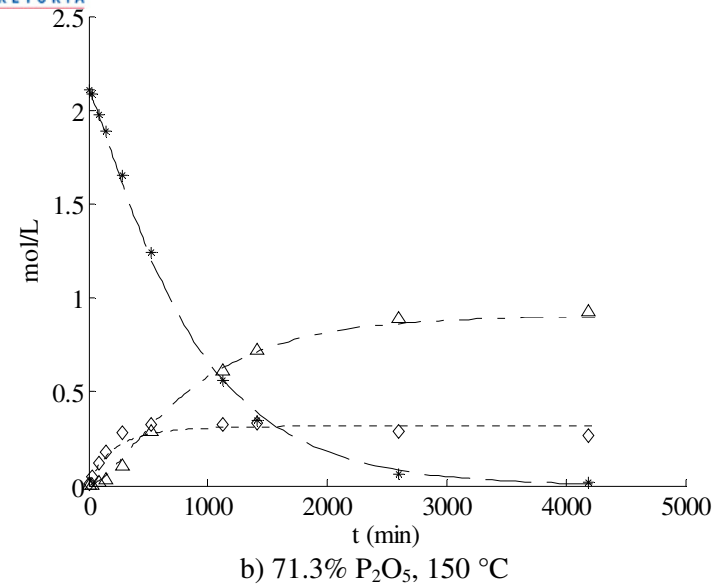
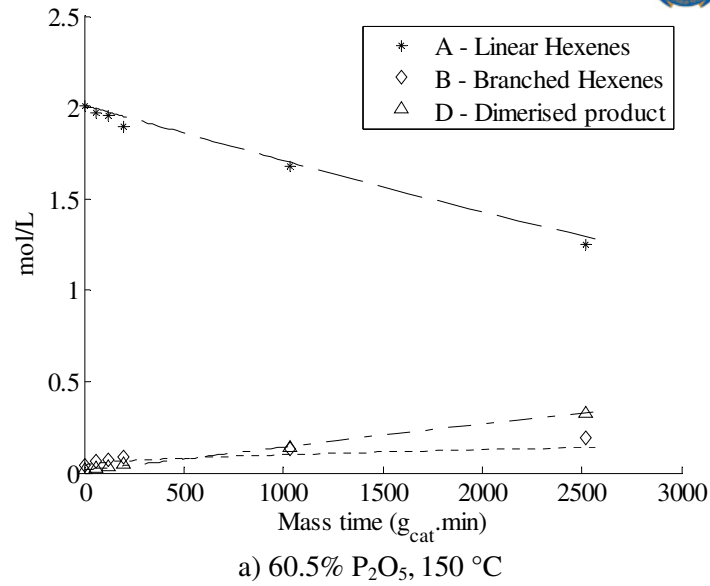


Figure 4-5: Rate of 1-hexene dimerisation for various acid strengths a) 60.5%, b) 71.3% and - c) 71.8% at 150 °C, with \* - linear hexenes, ◇ - branched hexenes and △ - total hexene depletion.

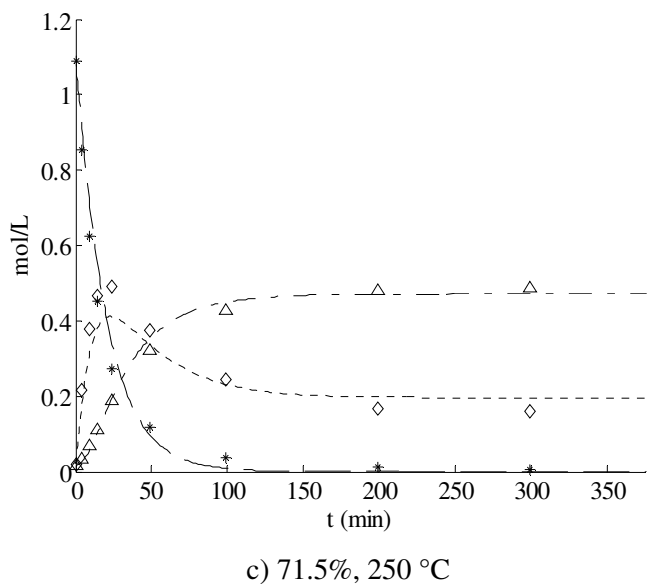
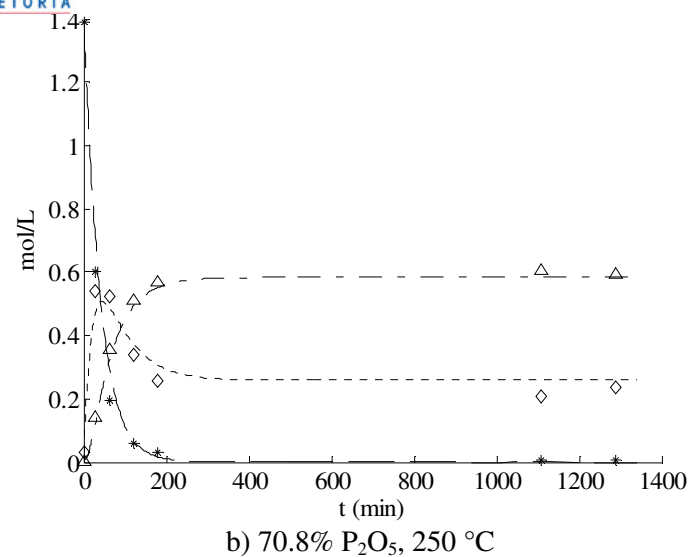
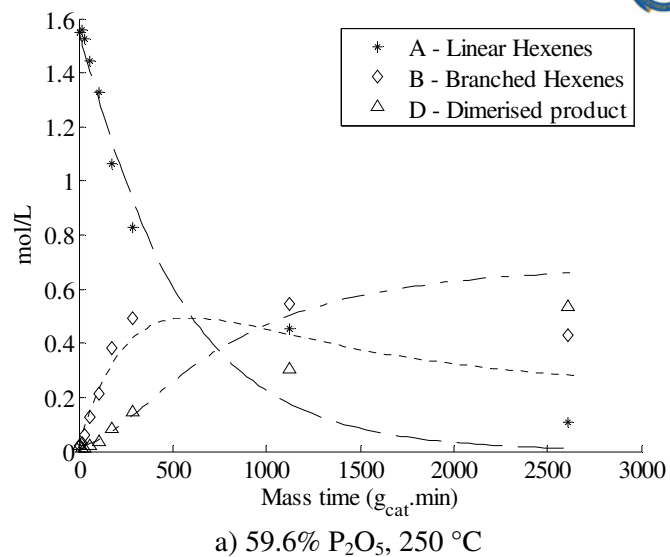
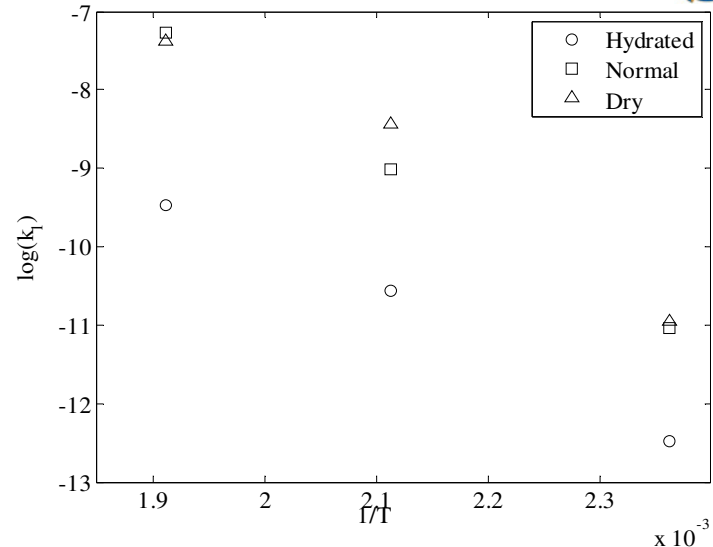
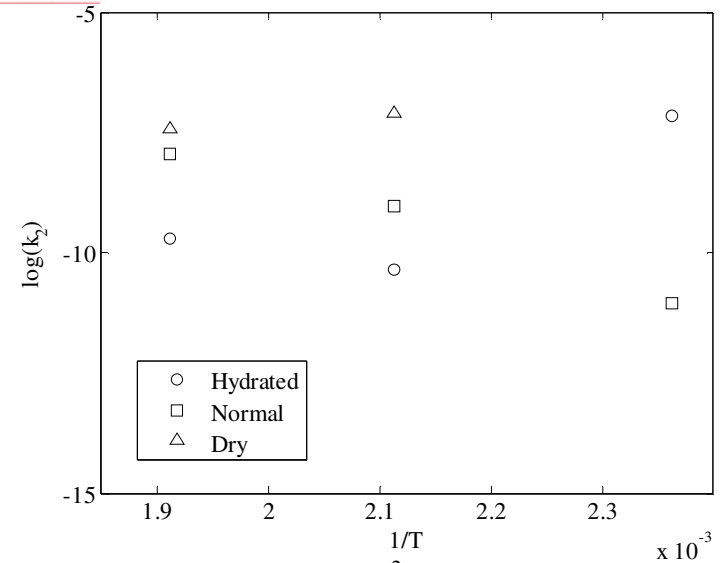


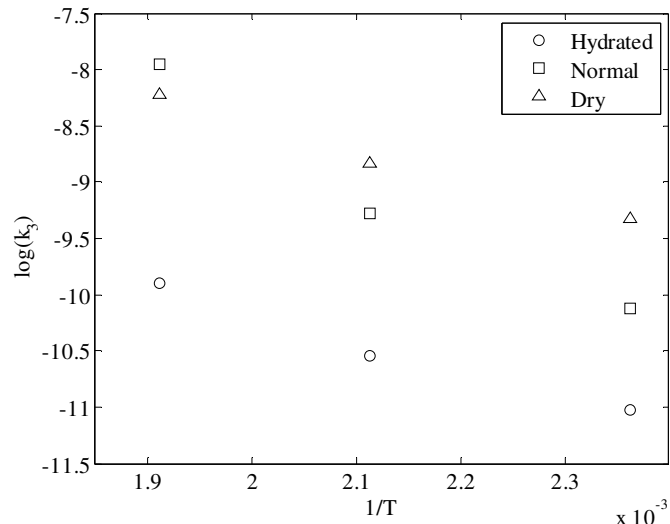
Figure 4-6: Rate of 1-hexene dimerisation for various acid strengths a) 58.4%, b) 73.1% - c) 73.7% at 250 °C, with \* - linear hexenes, ◇ - branched hexenes and △ - total hexene depletion.



a)  $k_1$  Skeletal isomerisation (L/min.g)



c) BHD  $k_2$  (L $^2$ /mol.min.g)



b) CD  $k_3$  (L $^2$ /mol.min.g)

Figure 4-7: Effect of the hydration of SPA on the rate constants,  $k_1$  – skeletal isomerisation,  $k_2$  – DBH and  $k_3$  – CD.



The trends seen in the dimerisation of hexenes at various acid strengths (Figure 4-4) and temperatures (Figure 4-7) indicate that an exponential dependency persists for both temperature and acid strength. The activation energy appears constant for both  $k_1$ ,  $k_3$  with some deviation in  $k_2$ , suggesting that the activation energy for the reaction is not affected by the acid strength and that the activation energies determined previously will still hold (Figure 3-16). It would therefore be appropriate to model the reaction rate in a similar fashion as that proposed by McClean (1987), Equation 2-9, but using an exponential dependency with acid strength on the rate constant.

To describe how the rate constants for the dimerisation of hexene are affected by the acid strength, Equation 4-2 was fitted to all the kinetic data gathered (Table 3-2 and Table 4-2) by minimising the AARE between the experimental and predicted concentrations by altering the pre-exponential constant,  $k_{x,o}$ , and the acid strength dependency,  $k_{x,A_A}$  (where  $A_A$  is the  $P_2O_5$  weight %). The activation energy was taken as predicted in Section 3.4.

$$k_x = k_{x,o} e^{-\frac{H_a}{RT} + k_{x,A_A} A_A} \quad 4-2$$

The resulting fitted parameters are shown in Table 4-4. It is evident that the rate of skeletal isomerisation and the DBH are more dependent on the acid strength than the CD. The model's predicted rate constants (Equation 4-2) correlate well with the rate constants derived from the fitting of the individual experiments. Previously the rate constants were fitted for each individual acid strength at a specific temperature (Figure 4-4 and Figure 4-7) whereas Equation 4-2 would allow for the regression of all data simultaneously. The parity plot between the resulting rate constants is shown in Figure 4-8, and the AARE was calculated to be 29%. This was expected, since some of the previously fitted parameters showed a negative activation energy (the dry reaction rate constant, Figure 4-7 c)), which was not allowed for in Equation 4-2.

Table 4-4: Pre-exponential constant and acid strength dependency of rate constants

	$k_{x,o}$	$k_{x,A_A}$
$k_1$ Skeletal isomerisation (L/min.g)	1.21	11.42
$k_2$ BHD ( $L^2/mol.min.g$ )	$3.59 \times 10^{-3}$	21.47
$k_3$ CD ( $L^2/mol.min.g$ )	$8.79 \times 10^{-4}$	8.39

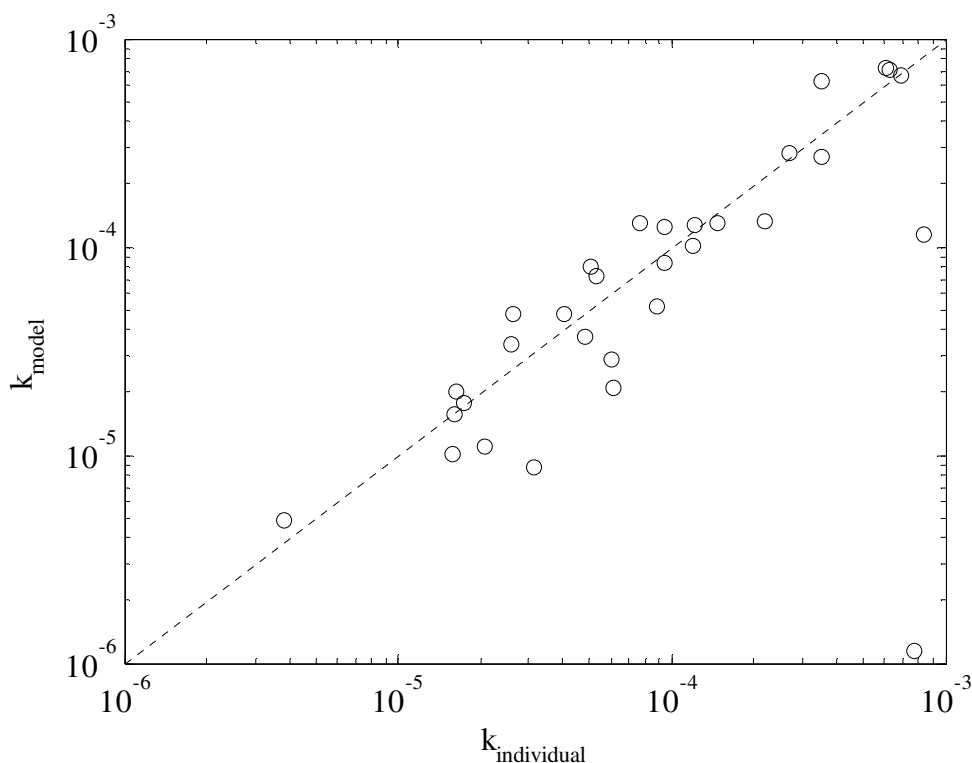
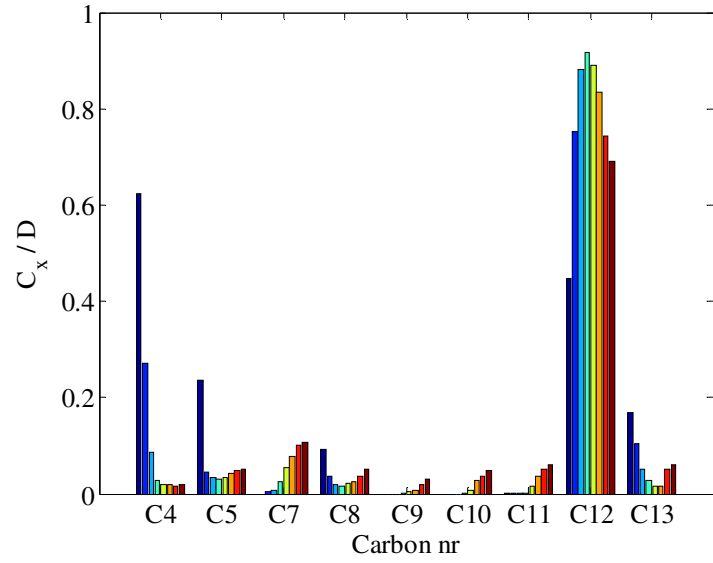


Figure 4-8: Comparison between the kinetic parameters modelled individually and the parameters of the model given in Equation 4-2.

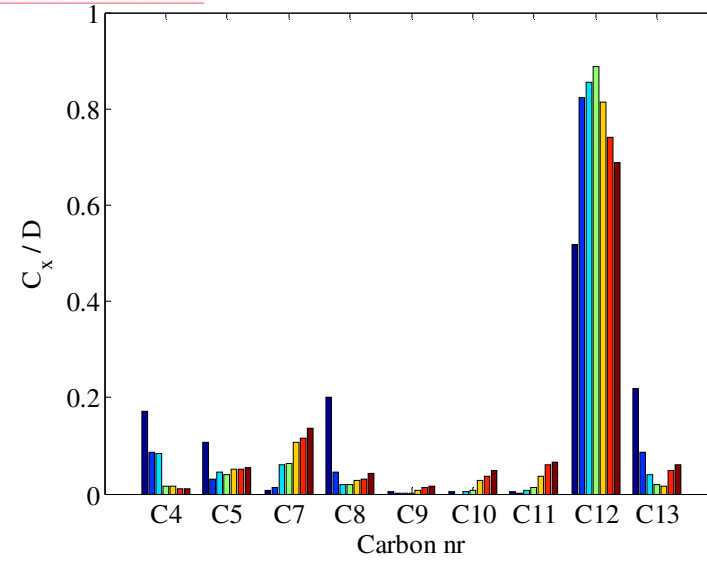
#### 4.2.3 Effect of acid strength on the product spectrum

If the product spectrum of the various acid strengths investigated is compared, the effect is not as obvious as it is with the reaction rate. The product distribution for various acid strengths was expressed as described in Section 3.3.2. The resulting product distribution for various acid strengths at 200 °C is shown in Figure 4-9 *a) -d)* and Figure 4-10.

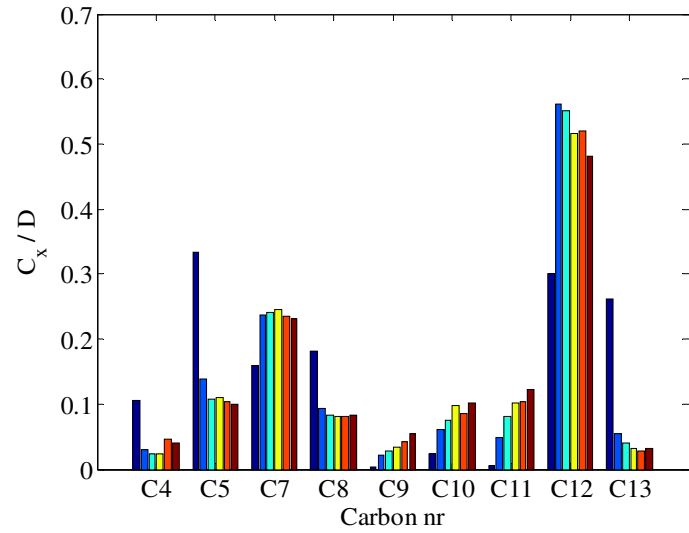
From the product spectrum of the catalyst where the acid was pre-treated at 600 °C, a higher selectivity toward dimerised product was evident (Figure 4-9 *a)*). This indicates that cracking is inhibited at lower acid strengths. However, when there is an increase in acid strength from 58.4% P<sub>2</sub>O<sub>5</sub> to 70.3% P<sub>2</sub>O<sub>5</sub>, this trend does not hold (Figure 4-9 *b) -d)*), as less cracking was seen in the case where the catalyst was washed and dried at 200 °C (Figure 4-9 *b)*) than in the cases where the catalyst was hydrated and dried (Figure 4-9 *c) & d)*). There is however a large jump in the free acid strength from the baked catalyst (600 °C, free acid = 0.4%), to the washed catalyst (free acid = 5.7%) and the hydrated/dried/untreated catalyst (free acid = 21.6%). This suggests that the free acid content affects the degree of cracking seen (i.e. less cracking is seen with lower free acid contents).



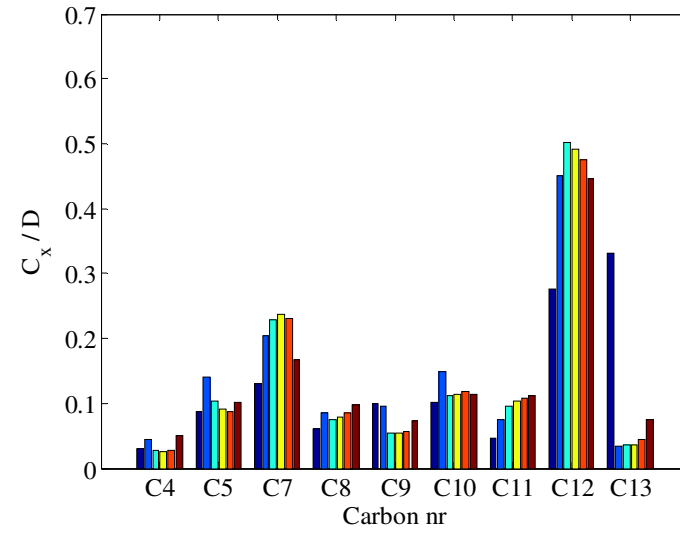
a) 49.8% P<sub>2</sub>O<sub>5</sub>



b) 66.4% P<sub>2</sub>O<sub>5</sub>



c) 59.6% P<sub>2</sub>O<sub>5</sub>



d) 70.8% P<sub>2</sub>O<sub>5</sub>

Figure 4-9: Effect of acid strength on the product spread at 200 °C, a) 49.8% to d) 69.4% P<sub>2</sub>O<sub>5</sub>.

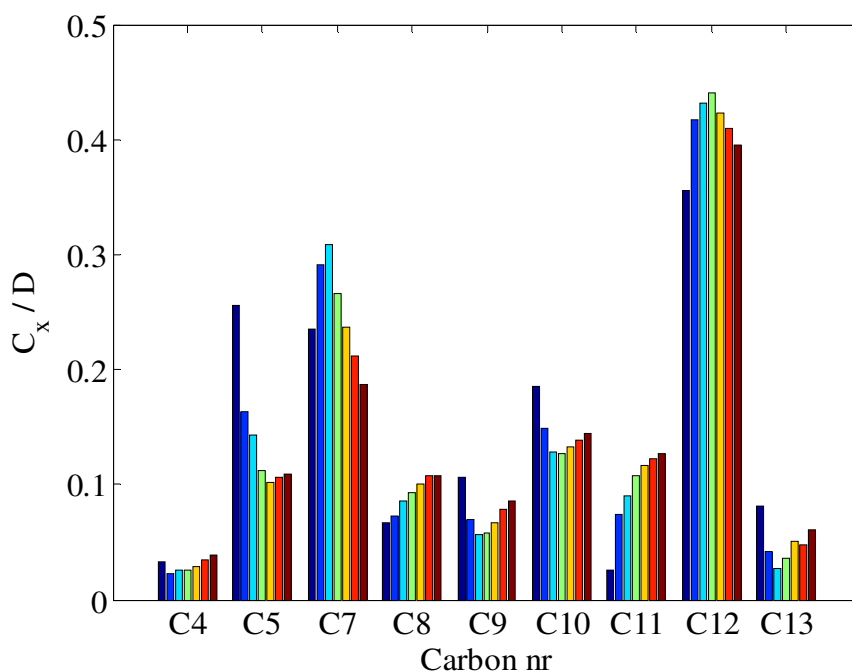
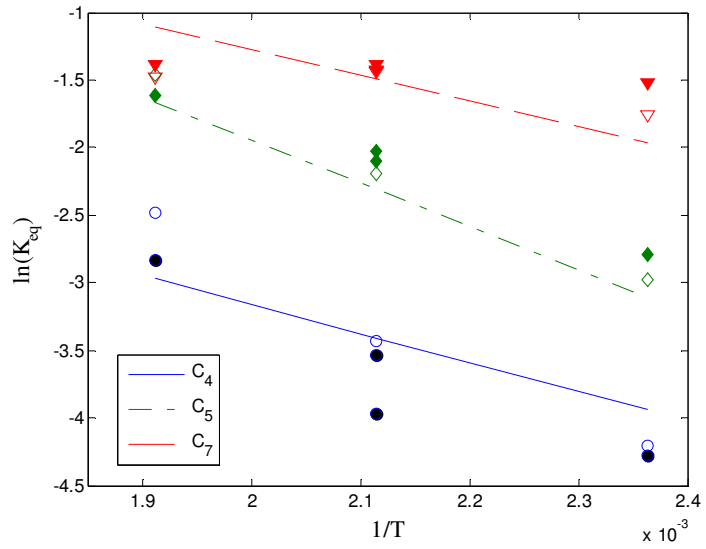
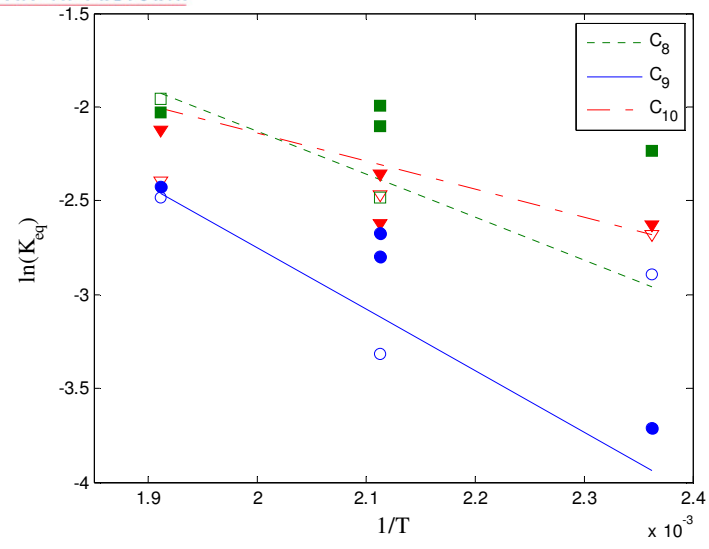


Figure 4-10: Effect of acid strength on the product at 200 °C, 71.5% P<sub>2</sub>O<sub>5</sub>.

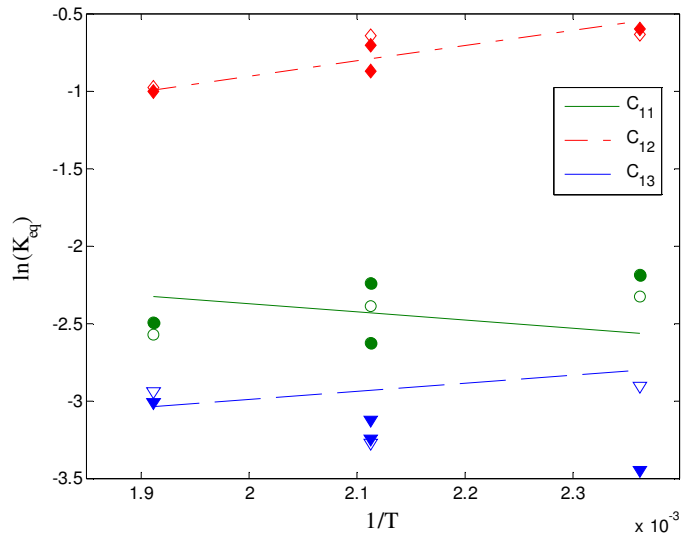
The reactions where the acid strength was altered by changing the hydration of the catalyst, with the same quantity of free acid, showed little deviation in the observed product spectrum obtained in Section 3.3.2 as seen in Figure 4-11. The deviation observed is similar to the deviation seen for the dimerisation of 1-hexene ( $\pm 70.8\%$  P<sub>2</sub>O<sub>5</sub>). This suggests that the degree of cracking observed during the dimerisation of 1-hexene is a function of the quantity of free acid on the catalyst and the reaction temperature, and is independent of the acid strength of the catalyst. The product distribution for 1-hexene oligomerisation over SPA is essentially controlled by two reaction rates: firstly, the rate of oligomerisation and secondly, the rate of cracking. The fact that the product distribution seems unaffected by acid strength indicates that the rate of oligomerisation is always the limiting reaction, even at high hydrations. Only by dramatically influencing the free acid content does the rate of cracking become prominent. Therefore the distribution of cracking products, at a specific temperature, can be seen to be always at a pre-determined equilibrium distribution.



a)  $\circ$ -C<sub>4</sub>,  $\diamond$ -C<sub>5</sub> and  $\nabla$ -C<sub>7</sub>



b)  $\square$  - C<sub>8</sub>,  $\circ$  - C<sub>9</sub> and  $\nabla$  - C<sub>10</sub>



c)  $\circ$ -C<sub>11</sub>,  $\diamond$ -C<sub>12</sub> and  $\nabla$ -C<sub>13</sub>

Figure 4-11: The effect of acid strength on  $\ln(K_{eq})$  versus the  $1/T$  where: 59.6% P<sub>2</sub>O<sub>5</sub> (open points), 71.8% P<sub>2</sub>O<sub>5</sub> (solid points).

### 4.3 Conclusions

It was shown that the reaction rate is highly dependent on the acid strength. With a decrease in the acid strength, the reaction rate decreased considerably. An exponential dependence of the rate constant was established with acid strength, which was integrated with the temperature dependence of the reaction rate (Equation 4-2). The proposed equation enabled the prediction of the reaction rate at all the gathered temperatures and acid strengths investigated. The resulting optimisation showed that the rate of skeletal isomerisation and DBH increased to the greatest extent with an increase in acid strength.

The carbon number distribution seemed to be unaffected by the extent of hydration, but it was seen that less cracking occurred as the free acid content of the catalyst dropped. This indicated that the fraction of cracking observed was a function of the free acid content and the reaction temperature, and was not dependent on the acid strength. Where the free acid content did not vary, the product distribution remained unaffected by the acid strength of the catalyst, meaning that rate of oligomerisation is limiting when predicting the product distribution and an equilibrium distribution of cracked products can be assumed.