

5 Product spectrum

The product formed from the oligomerisation of 1-hexene over SPA can be used as either lubricating oils, detergent production or fuel blending. Since it has previously been indicated that the 1-hexene does not form product longer than twenty the use for lubricating oils can directly be excluded. The degree of branching will however effect whether the product can be used for detergent production or petrol/jet/diesel blending.

Work done previously by De Klerk *et al.* (2006) indicated a difference between the degree of branching seen in the gasoline fraction that was dependent on the acid strength of the liquid phosphoric acid used when oligomerising C₄ olefins. These authors state that the acid strength of the phosphoric acid promotes skeletal isomerisation, oligomerisation as well as the cracking of oligomerised product. This makes it difficult to stipulate which reaction is promoted more significantly when influencing the degree of branching of the gasoline product. Trimerisation did not occur for the dimerisation of hexenes, indicating that only cracking will influence the degree of branching of the product. It was shown previously that the carbon distribution observed remained independent of the hydration/acid strength of the catalyst, and yet it was still shown that the rate of skeletal isomerisation and DBH was affected to a significant extent by the acid strength of the catalyst. This indicates that even though the carbon distribution remained unaffected, the degree of branching of the dimerised product might differ at various hydrations. Since this is an important measure of the quality of a fuel, the influence of the acid strength on the degree of branching of the dimerised product ought to be investigated. In previous chapters, the degree of branching of the dimerised product could not be measured owing to the significant overlapping in the GC analysis, therefore a more in-depth analysis of the sample would be needed to determine the impact of acid strength on the branching of the dimerised product.

5.1 Experimental

To determine whether the degree of branching of the dimerised product is affected by the acid strength of the catalyst, the degree of branching of the product was ascertained by proton nuclear magnetic resonance (¹H NMR) analysis for three different phosphoric acid strengths at 80% hexene conversion. The experiments were completed to obtain a degree of branching based on the hydration runs completed at 200 °C in Chapter 4 whereby the 1-hexene was dimerised with SPA pretreated at 200 °C for the following cases: 1) with only the latent water

present in the 1-hexene, 2) addition of 2000 ppm water to the reagent and 3) increasing the catalyst loading, and drying the 1-hexene with a mole sieve thereby increasing the ratio of the latent water to catalyst ratio. The reaction conditions for these three runs are shown in Table 5-1.

Table 5-1: Three reactions completed at 200 °C for analysis of the dimerised product.

	Sample 1	Sample 2	Sample 3
P ₂ O ₅ (W %)	62.0%	70.3%	71.4%
m _{cat} (g)	12.34	12.29	28.54
1-Hexene (g)	272.2	267.3	263.7
ppm H ₂ O	1461	150	80
Hexene conversion (%)	88.9%	80.3%	85.1%

To ensure that a clear indication of the product branching could be observed with the H NMR analysis, the dimerisation was completed without the addition of solvent. Since olefin content interferes with the branching measurement, the product was hydrogenated. The hydrogenation was done in a Parr autoclave reactor at 60 °C at a hydrogen pressure of 50 bars. The hydrogenation was completed using a 0.3% Pd Al₂O₃ catalyst with a particle size of 3 mm from Heraeus. The extent of the hydrogenation was determined from the Bromine number of the sample. A Mettler and Toledo DL 58, with the solvent and titrant prepared as specified by the manufacturer, were used for this purpose. The hydrogenation was found to be at least 97.8% complete, which was sufficient for H NMR testing.

After the hydrogenation it was necessary to separate the reagent from the products. A PiloDist 1000 was used to separate the mixture into two fractions for H NMR testing: 1) the gasoline fraction, boiling higher than C₆ paraffins (75 °C – 174 °C); and 2) the distillate, which was taken as the product boiling after n-decane (>174 °C) (De Klerk *et al.*, 2006).

5.2 Results and discussion

5.2.1 Acid strength

After the product was hydrogenated and fractionated into a gasoline and distillate fraction, both samples were sent for GC/MS analysis to gain an idea of the carbon number distribution. The resulting analysis is shown in Table 5-2 for the gasoline and the distillate fractions. The

GC/MS analysis shows no clear difference in the carbon number distribution dependent on the hydration of the catalyst (as indicated previously, Figure 4-11).

Table 5-2: Mole percentage carbon distribution from GC-MS for the a) gasoline and b) distillate cut.

<i>a)</i>		Gasoline cut		
Acid Strength		71.4%	70.3%	62.0%
$\leq C_5$		0%	0%	0%
C_6		1%	0%	0%
C_7		15%	5%	16%
C_8		15%	12%	17%
C_9		18%	16%	17%
C_{10}		37%	43%	35%
C_{11}		14%	22%	15%
C_{12}		0%	1%	0%
$\geq C_{13}$		0%	0%	0%

<i>b)</i>		Distillate cut		
Acid Strength		71.4%	70.3%	62.0%
$\leq C_9$		0%	0%	0%
C_{10}		3%	4%	5%
C_{11}		53%	53%	56%
C_{12}		35%	37%	35%
C_{13}		7%	4%	4%
C_{14}		1%	1%	0%
C_{15}		0%	0%	0%
C_{16}		1%	1%	0%
$\geq C_{17}$		0%	0%	0%

The gasoline and distillate fractions were sent for H NMR analysis to determine the fraction of CH_3 — bonds. An idea of the branching of the reaction products could then be determined from the average molecular weight of the sample (Table 5-3: a degree of branching of two indicates two methyl branches are present on the hydrocarbon).

Table 5-3: Degree of branching of fuel cut

Acid strength	Gasoline cut	Distillate cut
71.4%	2.35	2.95
70.3%	2.58	2.97
62.0%	2.35	3.00

This means that for the same conversion of hexenes the acid strength did not influence the product distribution for either the gasoline or diesel fraction (*i.e.* same extent of cracking) and that the acid strength also did not influence the degree of branching. This is similar to what was observed in Section 4.2.3 where the acid strength did not alter the carbon distribution obtained. This indicates that the only lever which will influence the carbon distribution is temperature (Section 3.3.2). This was however for a fairly small variance in the acid strength of SPA for this investigation.

One case in the literature where oligomerisation of naphtha range products have been calculated, is the thermal oligomerisation of a C₅/C₆ FT cut at 320 – 400 °C where the CH₃:CH₂ ratio was 0.4 to 1 (De Klerk, 2005b). The extent of oligomerisation was more severe than for this investigation, the final boiling point of the product was a 540 °C which if the normal boiling point of a hydrocarbon is assumed equates to a C₄₈ paraffin. The cetane number measured for the distillate fraction was though found to be between 41 and 48. If the correlation of O’Conner *et al.* (1992) is used to estimate the cetane number of the diesel fraction for this investigation the cetane was found to be 29. The low cetane is due to the high degree of branching observed in the distillate fraction, as such the distillate would mostly be viable as a jet fuel.

As for the degree of branching of the gasoline, data is available for the oligomerisation of butenes over SPA (Bekker and Prinsloo, 2009). The degree of branching found for the dimerised product, the C₈ fraction, was found to be 2.3 at 210 °C. If it is assumed that C₄ and C₆ dimerisation occurs through a branched intermediate the degree of branching should be similar for two dimerised fractions (C₈ and C₁₂ fractions respectively). During C₄ oligomerisation over SPA, trimerisation will occur to the distillate fraction (trimerisation) which was not observed for hexene. This would result that the degree of branching of the C₈ fraction is lower than observed for the C₁₂ fraction of the hexene dimerisation product (which was on average 3.0).

The degree of branching of the C₈ fraction (2.3) for C₄ oligomerisation is quite similar to gasoline fractions degree of branching for hexene dimerisation (on average 2.4). There are however some distinct differences between the two products: the gasoline fraction for the hexene dimerisation contained C₇-C₁₁ hydrocarbons formed predominantly from cracking and secondary oligomerisation whereas the C₈ fraction formed from dimerisation and is depleted by further oligomerisation as well as cracking to shorter chain olefins.

The quality of the hydrogenated gasoline fraction is highly dependent on the degree of branching and the carbon number. For a degree of branching between 2-3 the RON can vary between 50 to 101.8 over this carbon number, Table 5-4 (Daubert and Danner, 1987; Jones and Pujado, 2006). This states that the RON of the gasoline fraction is dependent on where the branching is positions. For a definitive description of the gasoline fractions quality, engine testing would be required.

Table 5-4: RON of C₇-C₁₀ paraffin dependent on the branching

Component	RON
Dimethyl pentane	83.1-91.1
Trimethyl butane	101.8
Dimethyl hexane	72.5
Trimethyl pentane	100
Dimethyl heptane	50.3
Trimethyl hexane	91
Trimethyl heptane	86.4

5.3 Conclusion

The effect of acid strength was tested by comparing the degree of branching seen for three different acid strengths at the same conversion of hexenes. A large degree of branching was evident in both the gasoline and distillate fractions. As such the cetane number of the distillate fraction was found to be 29, indicating that the distillate would be more viable as a jet fuel than a diesel. Engine testing of the gasoline fraction would be needed for a more clear indication of the RON of the hydrogenated gasoline.

For the range of acid strength investigated it was found, that the acid strength of the catalyst did not influence the degree of branching or the carbon distribution of the product. Therefore temperature is the most viable means of altering the carbon distribution of the product.

6 Conclusions

Kinetic data was gathered for the dimerisation of 1-hexene between 100 – 250 °C. To compensate for the differences in reactivity between linear and branched hexenes, the dimerisation was also completed for DMB. Due to the increased reactivity of branched olefins, a reaction mechanism was proposed that allowed for the skeletal isomerisation of linear hexenes, after which dimerisation/co-dimerisation occurs. It was concluded from the optimisation of the kinetic model that the reaction kinetics could be adequately modelled using a simple elementary kinetic model. Only the co-dimerisation of linear and branched hexenes (CD) and the dimerisation of branched hexenes (BHD) were needed to model the reaction rate accurately (with linear dimerisation found to be negligible). At low reaction temperatures the co-dimerisation of linear and branched hexenes dominated the reaction rate whereas at higher temperatures, the reaction rate was dominated by the dimerisation of branched hexenes. The reaction progression was seen to be controlled by the rate of skeletal isomerisation.

It became evident from the dimerisation of hexene using liquid ortho and pyro phosphoric acid that the acid strength has a strong influence on the activity of the catalyst. Experiments were conducted for various acid strengths of the catalyst. The acid strength of the catalyst was altered by either the hydration of the catalyst or by altering the free acid content of the catalyst. An exponential dependency of the rate constants on acid strength was observed at each acid strength from the prediction of the experimental data with an elementary kinetic model. This was incorporated into the rate constant which resulted in a kinetic model that could be used to predict the reaction rate at various acid strengths and temperatures.

It was also clear from the observed carbon distribution that carbon distribution evens out as soon as dimerisation occurs. Cracking and secondary dimerisation therefore occur much faster than the dimerisation of hexene. Higher temperatures promoted cracking, resulting in a flat carbon number distribution, whereas lower temperatures resulted in the formation of longer carbon chains. It was also seen that the product distribution was not dependent on the acid strength of the catalyst but was dependent on the free acid concentration of the catalyst. Since the free acid strength of the commercial catalyst does not differ during operation, the carbon number distribution is effectively only dependent on the reaction temperature.

The possibility still remained that increasing the acid strength could affect the branching of the produced product. Data on the dimerised product was then gathered for three acid

strengths for a constant temperature of 200 °C at the same conversion. The product was hydrogenated and fractionated and the degree of branching determined. A large degree of branching was evident in both the gasoline and distillate fractions, indicating that the dimerisation of hexenes would result in the production of a gasoline and jet fuel. However, it became clear from the degree of branching observed at various hydration states of the catalyst that the acid strength did not influence the degree of branching or the carbon distribution for both the gasoline and distillate fractions.