1-Hexene dimerisation over a solid phosphoric acid catalyst

Renier Bernhard Schwarzer
1 February 2012

A thesis submitted to the Faculty of Engineering, the Built Environment and Information Technology of the University of Pretoria, Pretoria, South Africa, in partial fulfilment of the requirements for the degree of Philosophiae Doctor (Chemical Engineering)

Supervisor: Prof. W. Nicol
Co-supervisor: Mrs E.L. du Toit
\[
\begin{bmatrix}
\cos 90^\circ & \sin 90^\circ \\
-\sin 90^\circ & \cos 90^\circ
\end{bmatrix}
\begin{bmatrix}
a_1 \\
a_2
\end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}
\]
http://www.xkcd.com/184
Abstract

Solid phosphoric acid is a catalyst used for the upgrading of light olefins into fuels. To delve into the mechanism of olefin dimerisation over the catalyst, the oligomerisation of 1-hexene was investigated over a wide range of operating conditions. The reaction progression of 1-hexene dimerisation over solid phosphoric acid was interpreted by means of kinetic experiments for both a linear hexene (1-hexene) and a branched hexene (2,3-dimethylbutene). The reaction rate for both reagents was described by using an elementary kinetic model. From the experimental data it was shown that the rate of dimerisation of branched hexenes was faster than the rate observed for linear hexene dimerisation. To correlate the two sets of kinetic data, the reaction network was expanded to incorporate skeletal isomerisation of 1-hexene with dimerisation only taking place by the co-dimerisation of linear and branched hexenes and the dimerisation of branched hexenes. The fit of the kinetic equation demonstrated that the reaction rate of 1-hexene is essentially controlled by the rate of skeletal isomerisation. Due to the large activation energy for skeletal isomerisation, low reaction temperatures favoured the co-dimerisation of linear and branched hexenes whereas at higher temperatures, the reaction rate was dominated by the dimerisation of branched hexenes. The product distribution indicated that, because of the fast rates of both cracking and secondary dimerisation (dimerisation of cracked products), the product distribution instantaneously reached a pseudo equilibrium after the dimerisation of hexenes. Therefore the carbon distribution was found to depend only on the reaction temperature, not on the residence time in the reactor.

Solid phosphoric acid is a supported liquid phosphoric acid where the condensed state of the acid, e.g. ortho phosphoric acid (H₃PO₄) and pyro phosphoric acid (H₄P₂O₇), is dependent on the quantity of water present in the reaction mixture. With a decrease in water content, the distribution of acid shifts and the ortho phosphoric acid becomes more condensed (H₄P₂O₇, H₅P₃O₉ etc.), i.e. high water content → low acid strength, low water content → high acid strength. The experiments completed at various degrees of catalyst hydration and free acid loading showed that the rate of reaction over solid phosphoric acid was dependent on the acid strength of the catalyst. The effect of acid strength on the reaction rate was integrated into the rate constants by means of an exponential dependency on acid strength. It was also shown that both the product distribution and the degree of branching remained unaffected by acid strength. The constant product indicates that the rate of cracking is limited by the rate of
oligomerisation of hexenes, irrespective of the acid strength of the catalyst. Since the product from the dimerisation of 1-hexene could be used as fuel, the quality of the desired fuel would therefore depend solely on the reaction temperature, not on the hydration of the catalyst.

The work performed in this thesis has been published in two peer-review articles:


Acknowledgements

My journey through postgraduate at the University of Pretoria was a memorable road to traverse, even though the journey is past the memories are treasured. I would like to thank Elizbe du Toit for her inspiration and encouragement to endure with my research, her guidance is greatly appreciated, together with Willie Nicol they kept me on the straight and narrow and steered the work to completion. Thanks also go out to Sasol Technology, whom sponsored this research, and to the colleagues whom helped direct, support and dispute the research in this thesis.
## Contents

Abstract ................................................................................................................................. iii

Nomenclature ...................................................................................................................... viii

List of Figures ......................................................................................................................... x

List of Tables ...................................................................................................................... xiii

1  Introduction ................................................................................................................. 1-1

2  Literature survey ......................................................................................................... 2-1

2.1  Oligomerisation: Product slate ................................................................. 2-1

2.2  Background: Oligomerisation of short chain olefins over SPA .................. 2-2

2.3  Oligomerisation of light naphtha olefins over SPA ....................................... 2-6

2.4  Solid phosphoric acid ...................................................................................... 2-8

2.5  Catalyst hydration ............................................................................................. 2-15

2.6  Reaction mechanism/network .......................................................................... 2-21

2.6.1  Classic carbocation mechanism ................................................................. 2-22

2.6.2  Phosphoric acid ester mechanism .............................................................. 2-23

2.7  Kinetic modelling of oligomerisation over acid catalyst ................................. 2-26

2.8  Closing remarks ................................................................................................. 2-32

3  Reaction Kinetics for 1-Hexene Dimerisation ......................................................... 3-1

3.1  Background .......................................................................................................... 3-1

3.2  Experimental ....................................................................................................... 3-2

3.2.1  Materials ....................................................................................................... 3-2

3.2.2  Experimental setup and method ................................................................. 3-2

3.2.3  Analysis ......................................................................................................... 3-5

3.3  Results & Discussion ........................................................................................... 3-7

3.3.1  Double bond and skeletal isomerisation ..................................................... 3-7

3.3.2  Dimerised and cracked products ................................................................. 3-18
3.4 Kinetic model ................................................................. 3-24
3.5 Conclusions .................................................................................. 3-33
4 Effect of Acid Strength on 1-Hexene Dimerisation ........................................ 4-1
  4.1 Experimental................................................................................... 4-1
    4.1.1 Acid strength characterisation .................................................. 4-1
  4.2 Results and discussion ......................................................................... 4-4
    4.2.1 Reaction rate for liquid ortho and pyro phosphoric acid .................. 4-5
    4.2.2 Reaction kinetics for various acid strengths of SPA ......................... 4-8
    4.2.3 Effect of acid strength on the product spectrum ............................. 4-18
  4.3 Conclusions ..................................................................................... 4-22
5 Product spectrum .................................................................................. 5-1
  5.1 Experimental................................................................................... 5-1
  5.2 Results and discussion ......................................................................... 5-2
    5.2.1 Acid strength .............................................................................. 5-2
  5.3 Conclusion ....................................................................................... 5-5
6 Conclusions .......................................................................................... 6-1
7 Bibliography .......................................................................................... 7-1
8 Appendix ............................................................................................... 8-1
  8.1 Product formation for the oligomerisation of DMB ............................... 8-1
  8.2 GCxGC results .................................................................................. 8-4
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Linear hexenes isomers, mol/L</td>
</tr>
<tr>
<td>A\textsubscript{A}</td>
<td>P\textsubscript{2}O\textsubscript{5} weight percentage (i.e. acid strength)</td>
</tr>
<tr>
<td>B</td>
<td>Skeletal hexene isomers, mol/L</td>
</tr>
<tr>
<td>C\textsubscript{x}</td>
<td>Concentration of molecule x, mol/L</td>
</tr>
<tr>
<td>D</td>
<td>Hexene depletion toward dimerised product, mol/L</td>
</tr>
<tr>
<td>E\textsubscript{a}</td>
<td>Activation energy, kJ/mol.K</td>
</tr>
<tr>
<td>k\textsubscript{1}</td>
<td>Kinetic constant for the rate of skeletal isomerisation, L/min.g</td>
</tr>
<tr>
<td>k\textsubscript{2,3}</td>
<td>Kinetic constant for the rate of dimerisation and co-dimerisation, L\textsuperscript{2}/mol.min.g</td>
</tr>
<tr>
<td>k\textsubscript{x,o}</td>
<td>Pre-exponential constant</td>
</tr>
<tr>
<td>k\textsubscript{x,A\textsubscript{A}}</td>
<td>Acid strength rate constant dependency</td>
</tr>
<tr>
<td>K\textsubscript{x}</td>
<td>Distribution of molecule x with reference to the hexene depletion</td>
</tr>
<tr>
<td>K\textsubscript{eq}</td>
<td>Experimentally determined equilibrium distribution of branched hexenes versus dimerised product</td>
</tr>
<tr>
<td>m\textsubscript{cat}</td>
<td>Weight concentration of catalyst in the reaction mixture, g/L</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}\textdegree</td>
<td>SPA base phosphoric acid strength, weight fraction P\textsubscript{2}O\textsubscript{5}</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5} (W %)</td>
<td>Acid strength of SPA</td>
</tr>
<tr>
<td>t</td>
<td>Time, min</td>
</tr>
<tr>
<td>T</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>W\textsubscript{Free acid}</td>
<td>Weight-free acid determined from titration, g</td>
</tr>
<tr>
<td>W\textsubscript{H\textsubscript{2}O}</td>
<td>Weight H\textsubscript{2}O in the reaction mixture, g</td>
</tr>
<tr>
<td>V</td>
<td>Volume of reaction mixture, L</td>
</tr>
</tbody>
</table>
Abbreviations

AARE  Absolute average relative error
IB    Iso-butene
CD    Co-dimerisation of linear and branched hexenes
CFPP  Cold Filter Plugging Point
DLH   Dimerisation of linear hexenes
DBH   Dimerisation of branched hexenes
DMB   2,3-dimethyl-2-butene
df    Film thickness
FID   Flame ionisation detector
FT    Fischer-Tropsch
i.d.  Inside diameter
GC    Gas chromatography
MON   Motor Octane Number
2M1B  2-Methyl-1-butene
2M2B  2-Methyl-2-butene
MS    Mass-spectrometry
RON   Research octane number
SPA   Solid phosphoric acid
FA    Free acid

Figure symbols

◊        Concentration of branched hexenes
*        Concentration of linear hexenes
△        Concentration of oligomerised product
List of Figures

Figure 2-1: Affect of space velocity on the conversion and RON for the oligomerisation of C4 olefins over SPA, ● – RON, ▲ - Conversion (De Klerk, *et al.*, 2004). ........................................ 2-6

Figure 2-2: Distribution of phosphoric acid as a function of P2O5 content (Jameson, 1959). .............................................................................................................................................. 2-12

Figure 2-4: Acid distribution with time when heating liquid phosphoric acid over and open flame at 200 °C (Ohtsuka & Aomura, 1962). ........................................................................ 2-13

Figure 2-5: Acid distribution over various kieselguhr supports when heated in a muffle furnace at 200 °C ................................................................................................................. 2-14

Figure 2-6: The effect of H4P2O7 (wt %) on the conversion of propylene (Zhirong *et al.*, 2000). .............................................................................................................................................. 2-18

Figure 2-7: Effect of acid strength and temperature on a) degree of branching of C8 olefins and b) gasoline-to-distillate ratio for C4 oligomerisation, for a constant residence time, over liquid phosphoric acid (De Klerk *et al.*, 2006). ........................................................................ 2-18

Figure 2-9: Effect of acid strength on the rate constant, ○ – 98% H3PO4, □ – 103% H3PO4, ◊ - 109% H3PO4 (Bethea & Karchmer , 1956). ........................................................................ 2-20

Figure 2-10: Various reactions that can occur during the oligomerisation of two olefins (Quan *et al.*, 1988). .............................................................................................................. 2-22

Figure 2-12: Phosphoric acid mechanism (Ipatieff, 1935) ................................................................................................................................. 2-24

Figure 2-13: The ester mechanism for a) one olefin reacting with an olefin or b) two esters dimerising. ........................................................................................................................... 2-25

Figure 2-14: Reaction mechanism as proposed by Farkas and Farkas (1942)........................... 2-25

Figure 2-15: Phosphoric acid ester mechanism for skeletal and double bond isomerisation. .............................................................................................................................................. 2-26

Figure 2-16: Reaction network for the oligomerisation of 2-methyl-1-butene (2M1B). 2-28

Figure 2-17: Reaction mechanism for McClean (1987). Reaction significance: → significant occurrence, → insignificant occurrence, → unknown occurrence, → normal route. .............................................................................................................................................. 2-32

Figure 3-1: Experimental setup .............................................................................................................. 3-3

Figure 3-2: 1-Hexene reaction progression at 250 °C versus weight time (gcat-min). Weight fraction of: ◊ = Linear hexene isomers; □ = skeletal hexene isomers and △ = overall hexene...
depletion (D). The stirrer speed is indicated by the open (500 rpm) and solid (1000 rpm) data points.

Figure 3-3: The reaction rate of 1-hexene at 250 °C (1000 rpm), where the catalyst was ground to 150 µm (open points) and 300 µm (closed points). Weight fraction of: ◊ = Linear hexene isomers; □ = skeletal hexene isomers and △ = overall hexene depletion.

Figure 3-4: Hexene isomers identified by GC-FID during the dimerisation of 1-hexene at 200 °C.

Figure 3-5: Isomers identified for 1-hexene dimerisation at 200 °C divided into a) linear hexenes, b) group A branched hexenes, c) group B branched hexenes and d) group C branched hexenes.

Figure 3-6: Cracking route of dimer to branched hexenes.

Figure 3-7: The reaction progression for 1-hexene dimerisation with reference to linear hexenes, branched hexenes and hexene depletion (dimerisation) at 200 °C.

Figure 3-8: Hexene isomers identified for the dimerisation of DMB at 200 °C.

Figure 3-9: Isomers identified for DMB dimerisation at 200 °C divided into a) linear hexenes, b) group A branched hexenes, c) group B branched hexenes d) group C branched hexenes.

Figure 3-10: The reaction progression for DMB dimerisation with reference to linear hexenes, branched hexenes and hexene depletion (dimerisation) at 200 °C.

Figure 3-11: Distribution of DMB at 150 °C for a) group B branched hexenes and b) group C branched hexenes (an insignificant amount of linear hexenes and group A hexenes was observed at 150 °C for the dimerisation of DMB over SPA).

Figure 3-12: Formation of oligomerised and cracked products for 1-hexene dimerisation.

Figure 3-13: Distribution of cracked and dimerised product for 1-hexene dimerisation.

Figure 3-14: Reaction mechanism for hexene dimerisation.

Figure 3-15: Kinetic fit of the dimerisation of 1-hexene, a) – d), and DMB, e) – h), with * - linear hexenes, ◊ - branched hexenes and △ - total hexene depletion.

Figure 3-16: Arrhenius relationship of fitted kinetic parameters, where the rate constant is for the various steps given in Figure 3-14, k₁ – skeletal isomerisation, k₂ – DBH and k₃ – CD.

Figure 3-17: ln(Kₑq) for each carbon number versus 1/T for 1-hexene dimerisation (excluding C₆) a) C₄, C₅ and C₇, b) C₈, C₉ and C₁₀ and c) C₁₁, C₁₂ and C₁₃.
Figure 3-18: ln(K_{eq}) for each carbon number versus 1/T for DMB dimerisation a) C_{4}, C_{5} and C_{7}, b) C_{8}, C_{9} and C_{10}, and c) C_{11}, C_{12} and C_{13}, the solid lines representing the carbon distribution observed for 1-hexene dimerisation (Figure 3-17). 3-32

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. 4-7

Figure 4-2: Reaction progression for the dimerisation of 1-hexene at 200 °C for acid strengths of 49.8% - 69.4% P_{2}O_{5}, with * - linear hexenes, ◊ - branched hexenes and △ - total hexene depletion. 4-9

Figure 4-3: Reaction progression for the dimerisation of 1-hexene at 200 °C for an acid strength of 70.3% P_{2}O_{5}, with * - linear hexenes, ◊ - branched hexenes and △ - total hexene depletion. 4-10

Figure 4-5: Rate of 1-hexene dimerisation for various acid strengths a) 62.5%, b) 72.9% and - c) 73.7% at 150 °C, with * - linear hexenes, ◊ - branched hexenes and △ - total hexene depletion. 4-14

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. 4-15

Figure 4-7: Effect of the hydration of SPA on the rate constants, k_{1} – skeletal isomerisation, k_{2} – DBH and k_{3} – CD. 4-16

Figure 4-9: Effect of acid strength on the product spread at 200 °C, a) 49.8% to d) 69.4% P_{2}O_{5}. 4-19

Figure 4-10: Effect of acid strength on the product at 200 °C, 70.3% P_{2}O_{5}. 4-20

Figure 4-11: The effect of acid strength on ln(K_{eq}) versus the 1/T where; 59.3% P_{2}O_{5} (open points), 70.3% P_{2}O_{5} (solid points). 4-21

Figure 8-1: Formation of oligomerised and cracked products for DMB oligomerisation. 8-2
Figure 8-2: Distribution of cracked and oligomerised product for DMB oligomerisation. 8-3
Figure 8-3: GCxGC results for 1-hexene product at a) 100 °C, b) 150 °C and c) 250 °C. 8-5
List of Tables

Table 2-1: Composition of feed to a catalytic polymerisation unit from Fischer-Tropsch, thermal cracking and catalytic cracking. ............................................................................................................ 2-3
Table 2-2: Effect of isobutene on oligomerisation rate and the quality of the hydrogenated produced fuel. ........................................................................................................................................... 2-4
Table 2-3: Unit conversion between % P_2O_5 and % H_3PO_4 ...................................................................... 2-11
Table 3-1: SPA C84/3 Properties .............................................................................................................. 3-2
Table 3-2: Kinetic experiments completed. ................................................................................................. 3-5
Table 3-3: Carbon analysis. ......................................................................................................................... 3-6
Table 3-4: Groupings of hexene isomers ..................................................................................................... 3-9
Table 3-5: Equilibrium distribution of hexene isomers from RGIBS reactor (Aspen™). 3-17
Table 3-6: Product spread for GCxGC at different temperatures. ............................................................... 3-23
Table 4-1: Experiments completed where the catalyst was hydrated/dried at various temperatures ................................................................................................................................................. 4-3
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 ................................................................................................................................. 4-4
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). ......................................................... 4-6
Table 4-4: Pre-exponential constant and acid strength dependency of rate constants...... 4-17
Table 5-3: Degree of branching of fuel cut ................................................................................................ 5-4
Table 5-4: RON of C_7–C_10 paraffin dependent on the branching .............................................................. 5-5