Impact of conjugated olefins on Ni-Mo-S/γ-Al₂O₃ catalyst deactivation and fouling of naphtha hydrotreaters

by

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Abstract

This dissertation investigates the reactions of conjugated olefins that lead to catalyst deactivation and fouling in naphtha hydrotreater reactors using a commercial Ni-Mo-S/γ-Al₂O₃ catalyst. The reactions were performed in a micro-scale fixed bed reactor system operated at 150-250°C, 3-4 MPa H₂, LHSV of 1-8 hr⁻¹ and a H₂/feed ratio of 392-1200 standard mL/mL.

During isoprene hydrogenation, an increase in dimerization activity with temperature was attributed to a higher activation energy of dimerization compared to hydrogenation.

Conjugated olefin content was also shown to impact oligomerization as an increase in the conjugated olefin content resulted in a decrease in hydrogenation product yield while the oligomerization activity and gum content increased.

By investigating different olefin structures, conjugation was shown to enhance dimerization/oligomerization while steric hindrance limited dimer/oligomer formation by limiting access and reactivity of the double bonds.

The addition of cyclohexene to 4-methylstyrene resulted in a significant loss in catalyst hydrogenation activity while the dimerization activity remained almost the same for a period of up to 30 days time-on-stream. The loss in catalyst activity can be attributed to a higher concentration of 4-methylstyrene when the overall conversion was lower, resulting in higher dimerization and gum formation. This in turn resulted in increased catalyst deactivation compared to the case of no cyclohexene in the feed. Reactor fouling was shown to be linked to
dimer and gum formation, as the pressure drop across the reactor increased with higher dimerization yield and gum formation. The increase in pressure drop was well described by a decreasing average reactor bed voidage caused by cumulative gum deposition within the catalyst bed.

An overall trend of increasing gum yield with increasing dimer yield is reported, suggesting that the dimers are precursors for gum formation. In addition, catalyst deactivation was linked to carbon deposition on the catalyst caused by dimer and gum formation; increased dimer and gum formation were accompanied by an increased carbon deposition and decreased BET surface area of the catalyst.

A kinetic model of the hydrogenation and dimerization of 4-methylstyrene over spent commercial Ni-Mo-S/γ-Al₂O₃ showed that hydrogenation has much lower activation energy (24.8 kJ/mol) than dimerization (68.2 kJ/mol).
Preface

The study presented in this thesis was completed by Ali H. Alzaid under the supervision of Professor Kevin Smith in the Department of Chemical and Biological Engineering at the University of British Columbia. The micro-scale reactor design, construction, set-up, and operation, catalyst activity measurement, and characterization, feed and product analysis and interpretation, kinetic modeling, literature review, and thesis preparation was performed by Ali H. Alzaid under the supervision of Professor Kevin Smith unless otherwise indicated. The main results of this thesis will be revised for submission to peer-reviewed journals.
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### Symbols

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<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$A_{BN}$</td>
<td>Bromide-bromate solution titration volume for the sample, mL</td>
</tr>
<tr>
<td>$A_{DV}$</td>
<td>Sodium hydroxide solution titration volume for the test, mL</td>
</tr>
<tr>
<td>$A_{GC-MS}$</td>
<td>GC-MS area under the peak</td>
</tr>
<tr>
<td>$a$</td>
<td>Effective cross-sectional area of one adsorbate molecule, m$^2$</td>
</tr>
<tr>
<td>$a_j$</td>
<td>Catalyst activity factor of reaction $j$, dimensionless</td>
</tr>
<tr>
<td>$B_{BN}$</td>
<td>Bromide-bromate solution titration volume for the blank, mL</td>
</tr>
<tr>
<td>$B_{DV}$</td>
<td>Sodium hydroxide solution titration volume for the blank, mL</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration, mol/L</td>
</tr>
<tr>
<td>$C_W$</td>
<td>Weight fraction, wt%</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Diffusivity of A in B, m$^2$/s</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Effective diffusivity, m$^2$/s</td>
</tr>
<tr>
<td>$\bar{D}_p$</td>
<td>Average particle diameter, m</td>
</tr>
<tr>
<td>$D_{p,i}$</td>
<td>Diameter of particle $i$, m</td>
</tr>
<tr>
<td>$d$</td>
<td>Pellet diameter, m</td>
</tr>
<tr>
<td>$d_e$</td>
<td>Equivalent pellet diameter, m</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Surface area average pellet diameter, m</td>
</tr>
<tr>
<td>$d_r$</td>
<td>Reactor diameter, m</td>
</tr>
<tr>
<td>$d_s$</td>
<td>Equivalent volume sphere pellet diameter, m</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy, kJ/mol</td>
</tr>
<tr>
<td>$F$</td>
<td>Molar flow, mol/h</td>
</tr>
<tr>
<td>$J_D$</td>
<td>Colburn $J$ factor, dimensionless</td>
</tr>
<tr>
<td>$K$</td>
<td>Equilibrium constant, dimensionless</td>
</tr>
<tr>
<td>$k$</td>
<td>Reaction rate constant, h$^{-1}$ for 1st order reactions and L/(mol·h) for 2nd order reactions</td>
</tr>
</tbody>
</table>
\( k' \) Reaction rate constant, L/(g·h) for 1st order reactions and L²/(mol·g·h) for 2nd order reactions

\( k_c \) Mass transfer coefficient for the diffusion from bulk liquid to external catalyst surface, h⁻¹

\( L_b \) Bed height, m

\( L_p \) Pellet length, m

m Mass, g

M Molarity, M

MW Molecular weight, g/mol

N Number of moles, mol

\( N_A \) Avogadro number, mol⁻¹

n Size of sample, dimensionless

\( n_r \) Reaction order, dimensionless

P Pressure, MPa

R Pellet radius, m

\( r \) Rate of reaction in terms of reactor volume, mol/(L·h)

\( r' \) Rate of reaction in terms of catalyst mass, mol/(g·h)

\( \text{Re}_p \) Modified Reynold's number, dimensionless

S Selectivity, wt%

\( S_A \) BET surface area, m²/g

\( Sc \) Schmidt number, dimensionless

\( Sh \) Sherwood number, dimensionless

T Temperature, °C

t Time, h

\( U \) Superficial velocity, m/s

V Volume, mL

\( V_m \) Volume adsorbed at monolayer coverage at STP, mL

W Catalyst weight, g

\( W_{BN} \) Weight of sample in the aliquot, g
$W_{DV}$ Weight of the diene value sample, g

$w_i$ Mass fraction of particle $i$, wt 

$X$ Conversion, 

$Y$ Yield, wt%

**Greek**

$P$ Single phase pressure drop across bed, kPa

$P_g$ Single phase pressure drop across bed for the gas flowing alone, kPa

$P_l$ Single phase pressure drop across bed for the liquid flowing alone, kPa

$\Delta P_{ig}$ Two phase pressure drop across bed, kPa

$\varepsilon_b$ Average reactor bed voidage, dimensionless

$\varepsilon_{cat}$ Catalyst bed voidage, dimensionless

$\eta$ Internal mass transfer coefficient, dimensionless

$\mu$ Viscosity, kPa·s

$v_0$ Volumetric flow rate of the feed, L/h

$\rho$ Density, kg/m³

$\sigma$ Standard deviation

$v$ Stoichiometric coefficient, dimensionless

$\phi_p$ Particle sphericity, dimensionless

$\Omega$ Overall catalyst effectiveness, dimensionless
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA</td>
<td>Amorphous aluminosilicates</td>
</tr>
<tr>
<td>ASAP</td>
<td>Accelerated surface area and porosimetry</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>BN</td>
<td>Bromine number</td>
</tr>
<tr>
<td>cC6</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>cC6=</td>
<td>Cyclohexene</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon-13 nuclear magnetic resonance</td>
</tr>
<tr>
<td>3-cus</td>
<td>3-coordinatively unsaturated</td>
</tr>
<tr>
<td>$C_{wp}$</td>
<td>Weisz-Prater's criterion</td>
</tr>
<tr>
<td>DPE</td>
<td>Diphenylethane</td>
</tr>
<tr>
<td>DV</td>
<td>Diene value</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid catalytic cracker</td>
</tr>
<tr>
<td>FIA</td>
<td>Fluorescent indicator adsorption</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>H/C</td>
<td>Hydrogen/carbon</td>
</tr>
<tr>
<td>HTGO</td>
<td>Hydrotreated light gas oil</td>
</tr>
<tr>
<td>ID</td>
<td>Internal diameter, mm</td>
</tr>
<tr>
<td>LHSV</td>
<td>Liquid hourly space velocity, h$^{-1}$</td>
</tr>
<tr>
<td>4-MS</td>
<td>4-methylstyrene</td>
</tr>
<tr>
<td>OBJ</td>
<td>Objective function</td>
</tr>
<tr>
<td>SAGD</td>
<td>Steam assisted gravity drainage</td>
</tr>
<tr>
<td>SE</td>
<td>Standard error</td>
</tr>
<tr>
<td>STP</td>
<td>Standard temperature and pressure</td>
</tr>
<tr>
<td>TOS</td>
<td>Time-on-stream, days</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra high purity</td>
</tr>
</tbody>
</table>
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To my father, Hussain

my mother, Ebtesam

my sister, Dr. Esra

my brother, Reda

To my beautiful wife, Dr. Doaa
Chapter 1: Introduction

1.1 Background

Canada ranks third in terms of proven oil reserves, with 173.2 billion barrels as estimated in 2014. This corresponds to 10.5% of the world's reserve as shown Figure 1.1 [1]. With established reserves of 167.2 billion barrels [2], Canadian oil sands constitute about 97% of the total oil reserves in Canada and more than 10% of the world's reserve. Once described by Time Magazine as "Canada's greatest buried energy treasure" [3], Canadian oil sands are a strategic energy source for North America.

The production of oil sands reached 2.29 million barrels/day in 2015. This number is estimated to increase to 3.95 million barrels/day by 2030 [4]. In terms of job market, about 290,000 people were working in the oil sands industry directly or indirectly in 2014 [5]. This makes oil sands a major driver of the Canadian economy.

Oil sand is a natural mixture that consists of 9-13% bitumen, 3-7% water, and 80-85% sand or other minerals of which 15-30% are fine particle (< 44μm in diameter) [6]. Figure 1.2 shows an image of crushed oil sands (a) and a high resolution image (240 (Horizontal) × 210 (Vertical) pixels) of 5 mm × 5 mm area of oil sands mixed with water (b). Bitumen is a heavy and viscous form of oil that contains a carbon/hydrogen ratio of ~1.5 [7]; higher than conventional oils.
As shown in Figure 1.3, there are three major deposits of oil sands in Canada, covering an area of 142,200 km², all located in northern Alberta: Athabasca, Cold Lake and Peace River. About 20% of the oil sands is located at ≤ 80 m depth and is recovered by surface mining. The remaining 80% is located at up to 760 m depth underground and is only recoverable by in-situ drilling production methods such as steam assisted gravity drainage (SAGD) [8].
Figure 1.2 (a) Crushed oil sand: a mixture of 9-13% bitumen, 3-7% water, and 80-85% sand or other minerals. [Reprinted with permission from Suncor Energy Inc., Copyright (2016)]. (b) Image of oil sand slurry (200 g oil sand (12.6 wt% bitumen) + 200 g water added, size of view area: 5 mm × 5 mm) from North Mine oil sand ore at 50°C [Reprinted with permission from John Wiley and Sons, Copyright (2014)] [9].

The surface mined oil sands upgrading consists of three main stages as shown in Figure 1.4. In the first stage, the oil is recovered by extraction and washing and then distilled to several fractions. This is followed by increasing the hydrogen/carbon (H/C) molar ratio by carbon rejection using fluid coker technology, or by H\textsubscript{2} addition, for example using LC-Fining, an ebullated bed process that hydrogenates hydrocarbon liquids over an expanded bed of catalyst where the catalyst turbulence and isothermal operation is achieved by liquid upflow [10]. Finally, hydrotreating is performed to remove metal, sulphur and other contaminants to produce a synthetic sweet crude oil [11]. Hydrotreating reactions are performed over a catalyst, a
substance that increases the reaction rate by providing a reaction path with a lower activation energy.

![Map of Alberta oil sands deposits.](image)

*Figure 1.3 Alberta oil sands deposits. [Reprinted with permission from Government of Alberta, Copyright (1995-2016)] [2].*

Typical liquid product properties from fluid coking are shown in Table 1.1. Naphtha is defined as a hydrocarbon fraction of crude oil with a boiling range of 30-200°C and consisting of a mixture of hydrocarbons with 5-12 carbon atoms [12]. The naphtha product from the fluid coker, shown in Figure 1.5, contains high amounts of olefins (20 wt%, bromine number=57-65.8 g/100
g) and diolefins (4.4 wt%, diene value=8.3-9.7 g I₂/100 g) [13]. The structures of the olefins and diolefins are not very well defined in the literature due to the presence of a large number of different structures causing analytical difficulties. This necessitates the investigation of different model olefin/diolefin structures in any test related to olefin/diolefin present in naphtha. Due to the presence of high amounts of olefins/diolefins, hydrotreating the naphtha product of the fluid coker without further processing leads to oligomerization reactions that produce carbonaceous deposits on the catalyst, leading to rapid catalyst deactivation, increase in reactor fouling, and eventually decreasing the operation time of the naphtha hydrotreater [7, 13]. Therefore, the naphtha product is pretreated to saturate the olefins and diolefins before passing to the naphtha hydrotreater units, as shown in Figure 1.5. This is achieved by hydrogenation at low temperature (< 250°C). Although the pretreater is operated at a relatively mild temperature, rapid catalyst deactivation and reactor fouling still occur and it is believed both are related to olefin or diolefin oligomerization [13]. This study, therefore, investigates the role of olefins/diolefins in catalyst deactivation and reactor fouling occurring in the pretreater operated at < 250°C temperature.

Table 1.1 Typical fluid coker product properties (Athabasca oil sands bitumen) [14].

<table>
<thead>
<tr>
<th>Product</th>
<th>Composition, wt%</th>
<th>Density, kg/m³</th>
<th>Sulphur, wt%</th>
<th>Nitrogen, ppmw</th>
<th>H/C ratio molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>14.1</td>
<td>782</td>
<td>1.68</td>
<td>237</td>
<td>1.76</td>
</tr>
<tr>
<td>Light gas oil</td>
<td>55.1</td>
<td>941</td>
<td>3.64</td>
<td>1600</td>
<td>1.55</td>
</tr>
<tr>
<td>Heavy gas oil</td>
<td>21.7</td>
<td>1002</td>
<td>4.33</td>
<td>3780</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Canadian oil sands upgrading system

Generic U.S. refinery system

Figure 1.4 Canadian oil sands upgrading system and an overview of a U.S. refinery system [5].
Due to its importance fundamentally and practically, hydrogenation of unsaturated hydrocarbons is well discussed in the literature. Different catalysts can be used for this process including noble metals (Ru, Pd, Pt, Ir and Cu) and metal sulphides (Ni, Mo, Co, W) [15-20]. Industrially, Co-Mo-S and Ni-Mo-S catalysts are mostly used for hydrotreating processes due to their strong resistance to poisoning from sulphur and nitrogen present in hydrotreating feeds [21], as shown previously in Table 1.1, and relatively lower costs [22]. Many studies have investigated naphtha hydrotreating reactions over MoS$_2$ catalysts for the purpose of producing ultra low sulphur gasoline to meet the maximum sulphur content regulation of 10 mg/kg set by Directive 2009/30/EC of the European Parliament and of the Council in 2009 [23-27]. However, these hydrotreating reactions are typically operated at $> 250^\circ$C temperature and $> 3.4$ MPa hydrogen pressure, targeting sulphur removal while minimizing aromatic hydrogenation and hydrogenolysis in order to preserve the value of the fuel [21]. Only few previous studies investigated hydrotreating reactions of olefins/diolenes over MoS$_2$ catalysts under relatively mild operating conditions ($< 250^\circ$C temperature and $\sim 3.4$ MPa) similar to the reaction of interest in this study. However, no studies were found examining both hydrogenation and dimerization/oligomerization reactions of olefins/diolenes and their kinetics over commercial
Ni-Mo-S/γ-Al₂O₃ catalyst at industrially relevant reaction conditions (< 250°C temperature, 3.4 MPa H₂ pressure, 1-2 hr⁻¹ liquid hourly space velocity (LHSV), and a constant H₂/feed ratio of 392 standard mL/mL). These studies are essential to understand the link between olefin/diolefin dimerization/oligomerization and catalyst deactivation and reactor fouling that leads to premature shutdown of hydrotreaters; an existing issue at commercial upgrading plants in Canada.

1.2 Thesis statement

The aim of this study is to investigate the reactions of olefins/diolefins that lead to catalyst deactivation and fouling in naphtha hydrotreater reactors using commercial Ni-Mo-S/γ-Al₂O₃ catalyst. Specifically, the study examines the effect of temperature, olefin/diolefin content and olefin/diolefin structure on the reactions in order to reduce oligomerization while maintaining high hydrogenation activity. Also, the relationship between oligomerization reactions, gum formation and reactor fouling is explored by measuring and comparing the oligomer yield/selectivity, gum content, and pressure drop across the reactor. Finally, the reaction kinetics for both hydrogenation and oligomerization reactions are developed to be used to predict the hydrogenation and oligomerization activities for process optimization purposes.

1.3 Research approach

The following research tasks were completed to achieve the research objectives:
- Hydrogenation of model diolefins, 2,5-dimethyl-2,4-hexadiene and isoprene, over Ni-Mo-S/γ-Al₂O₃ catalyst with and without a model olefin, 1-octene, to determine the onset of oligomer formation.

- Hydrogenation of a model diolefin, isoprene, using Ni-Mo-S/γ-Al₂O₃ over a temperature range of 150-250°C, and a feed diolefin content of 2.4-4.8 wt% (diene value of 9-18 g I₂/100 g) to investigate the effect of process conditions on dimer formation and reactor fouling.

- Hydrogenation of model olefins/diolefins with different structures with and without a model mono-olefin, 1-octene, over Ni-Mo-S/γ-Al₂O₃ to examine the effect of olefin/diolefin structure with and without mono-olefin addition on dimerization reactions.

- Hydrogenation of model conjugated olefins, 4- and α-methylstyrene, with and without a model cyclic mono-olefin, cyclohexene, using Ni-Mo-S/γ-Al₂O₃ over a period of 3, 12, 21 and 30 days time-on-stream (TOS) to investigate the link between dimerization reaction, catalyst deactivation, and reactor fouling.

- Hydrogenation of a model conjugated olefin, 4-methylstyrene, with a model olefin, cyclohexene, using Ni-Mo-S/γ-Al₂O₃ over 150-250°C temperature range and 2-8 h⁻¹ LHSV to estimate the reaction rates and activation energies for both hydrogenation and dimerization reactions.

Different model olefins/diolefins were investigated. The olefins/diolefins were diluted in an inert model solvent, decalin. Isoprene and 4-methylstyrene were selected as the main model reactants for further studies due to their dimerization tendency at industrially relevant reaction conditions (< 250°C temperature, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and a constant H₂/feed ratio of 392
standard mL/mL). The hydrogenation reactions were performed over fresh and spent sulphided commercial Ni-Mo-S/γ-Al₂O₃ catalysts (Criterion 424). The spent catalyst used was recovered from a Syncrude naphtha hydrotreater after shutdown. The catalysts were characterized for BET surface area, pore volume, and average pore width using N₂ adsorption and for carbon content using elemental CHNS analysis.

Thermal dimerization was also investigated using 8.4 wt% 4-methylstyrene in decalin as a feed at industrially relevant reaction conditions (250°C temperature, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and a constant H₂/feed ratio of 392 standard mL/mL), replacing the catalyst with SiC (mesh#80). Comparison with catalytic dimerization activity showed that dimerization was mainly catalytic; the dimer/4-methylstyrene yield ratio showed that catalytic dimerization was 10-13 times faster than thermal. A detailed analysis is included in Appendix A.

Two micro-scale fixed bed reactor systems were constructed and used for this study (length 50 cm; hot zone 30 cm; internal diameter 1.18 cm). The catalyst mass ranged from 0.5 to 4 g. The feed consisted of 2-20 wt% olefin/diolefin in a solvent (decalin or hydrotreated light gas oil). The operating conditions ranged from 150-250°C temperature, 3-4 MPa total pressure, 1-8 hr⁻¹ LHSV, and H₂/feed ratio of 392-1200 standard mL/mL. The liquid feed flow, inlet and outlet gas flow, reactor temperature, pressure and pressure drop across the reactor were monitored throughout the run. The liquid product was collected every 24 hours and analyzed using several techniques as following: gas chromatography mass spectrometry (GC-MS), gum content by jet evaporation (ASTM D381-12), olefin content by fluorescent indicator adsorption (ASTM D1319-10), bromine number/olefin content by electrometric titration (ASTM D1159-07), diene
value by maleic anhydride addition reaction (UOP 326-08), and carbon-13 nuclear magnetic resonance ($^{13}$C NMR).

To determine the onset of oligomer formation, each test at a certain set of operating conditions lasted for ~5 days TOS and were performed sequentially using the same catalyst bed for up to 45 days TOS. The investigation of the effect of process conditions and olefin/diolefin structures were carried out in the same sequential manner on the same catalyst bed with each test lasting for 3 days TOS at a certain set of operating conditions. For the investigation of the link between dimerization reaction, catalyst deactivation, and reactor fouling, each test at a certain set of operating conditions was completed using a new catalyst bed and lasted for 3, 12, 21 or 30 days TOS. For the reaction kinetic experiments, 12 runs were completed with a duration of 3 days TOS with a new catalyst bed used for each test. The runs were performed at 4 different temperatures, 150, 180, 200, and 250°C, and 3 different LHSV, 2, 4, and 8 h$^{-1}$ in order to estimate the reaction kinetics and activation energies for the hydrogenation and dimerization reactions.

1.4 Thesis outline

In the next chapter, studies related to olefin/diolefin structures and hydrogenation activity/selectivity, hydrogenation competition between mono-olefins and conjugated olefins/diolefins, role of catalyst properties on hydrogenation activity/selectivity, hydrotreating catalyst deactivation, and the kinetics of hydrogenation and dimerization of conjugated olefins are reviewed. The detailed experimental methods used in this study are reported in Chapter 3. In Chapter 4, the onset of oligomerization reactions was examined by hydrogenating 2,5-dimethyl-
2,4-hexadiene and isoprene over fresh and spent commercial Ni-Mo-S/γ-Al₂O₃ (Criterion 424). Significant dimer yields were detected when isoprene was used over spent Ni-Mo-S/γ-Al₂O₃ catalyst. Therefore, in Chapter 5, isoprene was selected as the model reactant and the reactions were performed over a spent Ni-Mo-S/γ-Al₂O₃ catalyst while changing process conditions, specifically temperature and isoprene content, to study the effect on dimerization activity and reactor fouling. In Chapter 6, hydrogenation reactions of different olefins/diolefins with and without mono-olefin addition were investigated over the spent Ni-Mo-S/γ-Al₂O₃ catalyst to study the effect of olefin/diolefin structure and mono-olefin addition on dimerization activity. From Chapter 6, 4-methylstyrene showed the highest degree of dimerization among all other olefins/diolefins tested and therefore it was selected as the model reactant in Chapters 7 and 8. The link between dimerization yield, catalyst deactivation and reactor fouling was examined in Chapter 7 by hydrogenating 4-methylstyrene over spent Ni-Mo-S/γ-Al₂O₃ catalyst for 3, 12, 21 and 30 days TOS. The effects of process conditions were also studied by changing the temperature (200-250°C), 4-methylstyrene content (4.2-8.4 wt% reflecting a diene value of 9-18 g I₂/100 g), model conjugated olefin structure (4- versus α-methylstyrene), and cyclic mono-olefin addition (cyclohexene). In Chapter 8, the kinetic parameters were estimated for hydrogenation and dimerization of 4-methylstyrene and the hydrogenation of cyclohexene. Finally, conclusions and recommendations are discussed in Chapter 9.
Chapter 2: Literature review

As stated in Chapter 1, many previous studies have examined hydrogenation of unsaturated hydrocarbons due to its importance fundamentally and practically. The studies cover a wide range of catalysts based on noble metals (Ru, Pd, Pt, Ir and Cu) and metal sulphides (Ni, Mo, Co, W) [15-20]. However, due to the presence of sulphur, nitrogen and other contaminants in hydrotreating feeds, which act as poisons for noble metal catalysts, most industrial catalysts are based on Co-Mo-S and Ni-Mo-S which resist poisoning at industrial conditions [16]. With tightening regulations on sulphur content in fuels, which was set to 10 mg/kg by Directive 2009/30/EC of the European Parliament and of the Council in 2009 [27], the number of studies examining naphtha hydrotreating reactions over MoS$_2$ catalysts has increased significantly [23-26]. Most of these studies, however, focus on typical hydrotreating conditions at $> 250^\circ$C temperature and $> 3.4$ MPa hydrogen pressure as required for hydrodesulphurization [21]. In the current study, the aim of the hydrotreater under investigation is to saturate the olefins/diolefins over MoS$_2$ catalysts under relatively mild operating conditions ($< 250^\circ$C temperature and $\sim 3.4$ MPa) to prevent oligomerization, catalyst deactivation and reactor fouling in the subsequent hydrotreater reactor that aims to remove sulphur, nitrogen, and other contaminants. Few studies are reported in the literature that focus on olefin/diolefin hydrogenation over MoS$_2$ catalysts under relatively mild operating conditions ($< 250^\circ$C temperature and $\sim 3.4$ MPa) and these studies are reviewed in this chapter.

The following literature review focuses on studies discussing the effect of olefin/diolefin structure and the role of catalyst properties on hydrogenation activity and selectivity, the
competition between the olefin/diolefin and mono-olefin during hydrogenation reactions, hydrotreating catalyst deactivation mechanisms, and hydrogenation and dimerization reaction kinetics.

2.1 Olefin/diolefin structure and hydrogenation activity/selectivity

Okuhara et al. [19] studied the selectivity of the isoprene hydrogenation reaction over MoS$_2$ catalyst (T=room temperature, P=4.3 kPa H$_2$, reactor: 300 mL closed circulating system). The reaction resulted in higher selectivity towards 2-methyl-1-butene (77.0%) than 3-methyl-1-butene (20.6%). This indicates that the double bond further away from the methyl group adsorbs more strongly to the catalyst compared to the double bond adjacent to the methyl group resulting in the higher selectivity to 2-methyl-1-butene compared to 3-methyl-1-butene. This was explained by the steric hindrance effect of the methyl group on the adsorption of the isoprene over the catalyst. This highlights the importance of molecular structure in determining the reactivity and product distribution of diolefin reactions and is a subject of interest in the present study focused on identifying the causes of the oligomerization reactions. The study also noted that after isoprene is consumed, isomerization of 2-methyl-1-butene proceeds to form 2-methyl-2-butene whereas 3-methyl-1-butene does not isomerize significantly.

Hubaut et al. [28] confirmed the results obtained by Okuhara et al. [19] in their study of the activity of olefins/diolefins using MoS$_2$/γ-Al$_2$O$_3$ catalyst pretreated with H$_2$ at different temperatures. Isoprene hydrogenation was performed at 50°C temperature, 101.3 kPa H$_2$ pressure, 38 mol/mol H$_2$/feed ratio, using a packed bed reactor (LHSV was not reported). The study reported that the reaction is more selective towards 2-methyl-1-butene (18.5%) than 3-
methyl-1-butene (negligible quantity). Other products obtained were the hydrogenated product isopentane (64%), and the isomerized product 2-methyl-2-butene (16%). As shown in Table 2.1, the study also found that the reactivity of isoprene and 1,3-pentadiene (conjugated diolefins) were 2-3 times higher than that of 1,4-pentadiene (non-conjugated diolefin), 1,3-cyclohexadiene (cyclic-diolefin) and 2-methyl-2-butene (mono-ethylenic olefin). This was explained by the low reactivity of the non-conjugated diolefin and the steric hindrance in the cyclic diolefin. No further mechanistic details were provided.

Table 2.1 Olefin/diolefin hydrogenation activities over MoS2/γ-Al2O3 catalyst [28].

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Structure</th>
<th>Temperature, K</th>
<th>Hydrogenation activity, 10^3 mol/(g·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td><img src="image" alt="Structure" /></td>
<td>323</td>
<td>30</td>
</tr>
<tr>
<td>1,3-pentadiene</td>
<td><img src="image" alt="Structure" /></td>
<td>323</td>
<td>35</td>
</tr>
<tr>
<td>1,4-pentadiene</td>
<td><img src="image" alt="Structure" /></td>
<td>353</td>
<td>8</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td><img src="image" alt="Structure" /></td>
<td>353</td>
<td>14</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td><img src="image" alt="Structure" /></td>
<td>423</td>
<td>7</td>
</tr>
</tbody>
</table>
2.2 Hydrogenation competition between conjugated olefins/diolefins and mono-olefins

Due to the presence of 20 wt% olefin (bromine number=57-65.8 g/100 g) in the fluid coker naphtha, as discussed earlier in Chapter 1, it is important to investigate the effect of the presence of mono-olefin in the feed during hydrogenation reactions. The competition between conjugated olefin/diolefin and mono-olefin hydrogenation reactions was discussed in some studies. All the studies reviewed agree that the rate of conjugated olefins/diolefins hydrogenation is always faster than that of mono-olefins. Nijhuis et al. [29] found that the rate of hydrogenation of styrene was 3.5x’s faster than that of 1-octene at 50°C and 1.6 MPa (Feed: 0.86 mol/L styrene or 0.79 mol/L 1-octene in toluene, catalyst: 0.19-0.21 g/L Pd(0.4-0.5wt%)/Al₂O₃, reactor: 500 mL batch, 1500 rpm stirring speed). The hydrogenation rates of cyclopentadiene (5wt%) and styrene (5wt%) were reported to be 6.6 and 3.9 times higher than that of 1-hexene (3 wt%) at 60°C and 2 MPa (solvent: n-heptane, catalyst: trilobe Pd(0.3 wt%)/Al₂O₃, reactor: semi-batch) [30]. This was explained by the stronger electrophilic character of conjugated olefins/diolefins [28]. The carbocation formed from conjugated olefin/diolefin during electrophilic addition is stabilized by resonance and therefore it is easier to form than the mono-olefin carbocation intermediate. The higher reactivity of conjugated olefins/diolefins was also attributed to the stronger adsorption on the catalyst compared to mono-olefins [30].

2.3 Role of catalyst properties on olefin/diolefin reaction activity and selectivity

In their study of isoprene hydrogenation over MoS₂/γ-Al₂O₃, Wambeke et al. [20] reported that the active sites for hydrogenation were the 3-coordinatively unsaturated (3-cus) Mo ions in the
edge of the (1\bar{0}10) plane of the MoS\textsubscript{2} slab as shown in Figure 2.1 (a). These active sites have 3 vacancies and one unsaturated sulphur atom as shown in Figure 2.1 (b).

![Diagram](image)

Figure 2.1 (a) Top and side views of a hexagonal MoS\textsubscript{2} showing the active sites location. (b) Hydrogen adsorption to a 3 coordinatively unsaturated Mo atom [reprinted with permission from Elsevier, Copyright (1988)] [20].

Jalowiecki et al. [31] reached the same conclusion for the hydrogenation of isoprene over unsupported MoS\textsubscript{2}. In addition, their study found that the active sites for the isomerization of cis-1,3-pentadiene were the 2- and 4-cus atoms on the edge of the (1\bar{0}10) plane of the MoS\textsubscript{2} slab. Prior to this study, Okuhara et al. [19] noted that the isomerization reaction proceeds via a carbocation mechanism on the sulphur layer of the MoS\textsubscript{2} crystal. Sufficient proton activity is available on the sulphur layer to form a tertiary carbocation intermediate from 2-methyl-1-butene which is then converted to 2-methyl-2-butene. Yang and Satterfield [32] further explained that H\textsubscript{2}S dissociative adsorption on Ni-Mo-S/\gamma-Al\textsubscript{2}O\textsubscript{3} can convert a sulphur vacancy to a -SH group and a Bronsted acid site, as shown in Figure 2.2. The study also stated that the added P\textsubscript{2}O\textsubscript{5}
promoter can be a source of Bronsted acid sites. These results are very critical to the current study as they confirm the presence of Bronsted acid sites which can donate a proton to the olefin/diolefin to form an allylic carbocation; the proposed intermediate for dimer formation, as discussed in later chapters.

![Figure 2.2 H₂S dissociative adsorption and Bronsted acid formation](image)

Kasztelan et al. [33] studied the site structure sensitivity of diolefin hydrogenation and isomerization over MoS₂/γ-Al₂O₃ catalysts at 50°C, and confirmed the conclusions by Wambeke et al. [20] and Jalowicki et al. [31]. The study also claimed that the alumina support did not contribute to the reactions as it was poisoned by the MoS₂ phase.

However, another study by Perez-Martinez et al. [34] claimed that modifying the Si/(Si+Al) ratio of CoMo catalysts supported on amorphous aluminosilicates (ASA) played a role in changing the reaction activity in the hydrotreatment of synthetic fluid catalytic cracker (FCC) naphtha (20 wt% olefin in n-heptane) at 250°C and 17 MPa. The study noted that increasing the Si/(Si+Al) ratio increased the total acidity up to 50% Si/(Si+Al). It was also found that as Si/(Si+Al) ratio increased, the activity of the acid reactions was enhanced (alkylation, isomerization and cracking) while the activities of the hydrodesulphurization and olefin hydrogenation reactions
were reduced. The study also reported the production of 1 wt% oligomers at the conditions tested. This study confirms the role of acidity in oligomerization and supports the dimerization reaction mechanisms proposed in later chapters which depend on allylic carbocation formation by reaction with a Bronsted acid. Although this study reported the production of oligomers at 250°C and 17 MPa, the study only focused on olefin hydrogenation and did not investigate the reaction mechanism for oligomerization or draw a relationship between oligomer production and catalyst deactivation and reactor fouling.

2.4 Hydrotreating catalyst deactivation

Catalyst deactivation is one of the greatest factors that influence the design and operation of industrial catalytic reactors. In general, catalyst deactivation can be classified into three main categories: chemical, which includes poisoning and loss of catalytic phases, thermal (sintering), and mechanical, which includes physical damage and fouling [21].

Poisoning occurs when impurity species strongly chemisorb to active catalytic sites. This results in blocking of active sites from reacting species, affecting adsorption ability of neighboring active sites, changing surface structure, blocking interaction between reacting species, and finally reducing the rate of reacting species surface diffusion [21]. Common poisons include Group VA, VIA, VIIA species (N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I), heavy metals (As, Pb, Hg, Bi, Sn, Zn, Cd, Cu, and Fe), and multiple bond chemisorbing molecules (CO, NO, HCN, benzene, acetylene, and unsaturated hydrocarbons) [35]. Poisoning can be selective, non-selective, or anti-selective. In selective poisoning, poisons adsorb to the active sites preferentially causing high loss of activity at low poison concentration. In non-selective poisoning, the loss of catalyst
activity is proportional to the poison concentration. In anti-selective poisoning, the less active sites are blocked initially causing very low loss of activity at low poison concentration. In the current study, the catalyst is Ni-Mo-S/\(\gamma\)-Al\(_2\)O\(_3\) which resists poisoning in industrial process conditions [16] and therefore poisoning is not a relevant catalyst deactivation mechanism in the case of premature hydrotreater shutdown.

Loss of catalytic phases can occur by reaction of gas with active metals to form volatile products or by reaction of fluid or catalyst components (support or promoter) with active metals forming non-active products [21]. However, this deactivation mechanism is unlikely to occur during naphtha hydrotreating.

Thermal degradation or sintering occurs at high reaction temperatures, typically >500°C. It involves (A) atomic or (B) crystallite (consisting of several metal atoms) migration over the support leading to crystallite growth and loss of surface area [35, 36]. Figure 2.3 shows a model for sintering. In crystallite migration, the entire crystal migrates over the support, colliding and merging with other crystallites to form larger crystallites. In atomic migration, atoms detach from a crystallite, migrate over the support and attach to larger crystallites. In this study, the reactor is operated at < 250°C so sintering is not a relevant deactivation mechanism.

Physical damage may occur to catalysts in terms of crushing, attrition or erosion. This leads to loss of active metals and surface area and therefore the catalytic activity [35].
Finally, catalyst fouling, the deactivation mechanism relevant to this study, falls under both chemical and mechanical deactivation categories. Fouling occurs when large molecular weight hydrocarbons or coke form and deposit on the surface of the catalyst. These materials deactivate the catalyst by physically covering active sites and blocking access to catalyst pores (fouling), or by strongly chemisorbing to active sites (poisoning). Figure 2.4 shows an illustration of catalyst fouling by carbon deposition.
Coke can form by free radical addition reactions involving olefins, diolefins and alkanes at high temperature (365-434°C) [7]. However, this coke formation mechanism is not relevant since the reactor in this study is operated at < 250°C.

For supported metal sulfide catalysts, it has been stated in previous studies that coke formation primarily involves the reaction of coke precursors, such as olefins, diolefins and aromatics, over acidic catalytic sites [37-39]. As shown in Figure 2.5, Bartholomew explained the reaction mechanism for coke formation as follows: a) olefin dimerization, b) olefin cyclization to form benzene, and c) benzene oligomerization to form poly-aromatics (coke). Olefin dimerization starts with the formation of a secondary carbocation by reaction with a Bronsted acid (1). The carbocation reacts with another olefin to form a secondary carbocation dimer (2). The carbocation dimer reacts with a Bronsted base to form the final dimer (3). Olefin cyclization starts by the reaction of a conjugated diolefin with a primary carbocation to form an allylic carbocation (4) which reacts with a Bronsted base to form a triene (5). The triene undergoes cyclization reaction to form a substituted cyclohexadiene (6). The substituted cyclohexadiene reacts with a primary carbocation to form a tertiary carbocation (7) which eventually forms a substituted benzene by reaction with a Bronsted base (8). To form coke, the benzene reacts with a Bronsted acid to form an allylic carbocation (initiation step 9). Then the allylic carbocation reacts with other benzene molecules to form a polynuclear aromatic carbocation (propagation steps 10-13). The coke formation terminates by reaction with a Bronsted base to form a polynuclear aromatic molecule (coke) (14).
As discussed earlier, the Bronsted acid sites of the Ni-Mo-S/γ-Al₂O₃ catalyst can donate a proton. This aids in forming the intermediate carbocation required for dimer/oligomer formation from the conjugated olefin/diolefin present in the naphtha during hydrotreating. Coke or coke precursor formation will be confirmed in this study and linked to catalyst deactivation and reactor fouling.

Weissman and Edwards [40] studied the deactivation of hydrotreating catalysts, namely Ni-Mo-S and Co-Mo-S supported on alumina, under industrial reaction conditions (T=280-390°C, P=5.5 MPa, LHSV= 2 h⁻¹, and H₂/feed=360 standard cm³/cm³). In the case of naphtha hydrotreating, the paper stated that the catalyst deactivation was mainly due to deposition of a relatively low density carbon on the catalyst, blocking the active sites. It was also reported that changes in the structure of MoS₂ did not result in activity loss.

Another study by Lamberov et al. [41] investigated the deactivation of Pd supported on Al₂O₃ catalyst for the hydrogenation of diolefins (T=30-80°C, P=4.7 MPa, LHSV= 2-4 h⁻¹, and H₂/feed=100:1 to 300:1). The study found that catalyst deactivation in the upper part of the reactor was mainly due to the accumulation of poisons, namely Cr, Cu, Mn, Mg, and Fe compounds. In the lower part of the reactor, the catalyst deactivation was mainly attributed to the blockage of active sites by organic deposits.
a. Polymerization of Olefins

Step 1: Reaction of olefin with Bronsted acid to form secondary carbenium ion:
\[ H_2C=CHCH_3 + HX \rightleftharpoons CH_3-\stackrel{\cdot}{CH}CH_3 + X^- \] (1)

Step 2: Condensation reaction of a C2 carboxylation with a C2 olefin to form a.
condensed, branched C6 product with a carbenium ion:
\[ CH_3-\stackrel{\cdot}{CH}CH_3 + H_2C=CHCH_3 \rightleftharpoons CH_3-\stackrel{\cdot}{CH}CH_3 + \] (2)

Step 3: Reaction of carbenium ion with Bronsted base to form olefin:
\[ CH_3-\stackrel{\cdot}{CH}=CH_2+X^- \rightleftharpoons CH_3-\stackrel{\cdot}{CH}CH_3+HX \] (3)

b. Cyclization from Olefins

Step 1: Formation of an allylic carboxylation ion by reaction of a diene with a.
primary carboxylation ion:
\[ R_1^+ + R_2 \cdot CH=CH \cdot CH=CH \cdot CH_3 \rightleftharpoons R_2H + (R_2 \cdot CH=CH \cdot CH=CH \cdot CH_3)^+ \] (4)

Step 2: Reaction of an allylic carboxylation ion with a Bronsted base to form a triene:
\[ X^+ + (R_2 \cdot CH=CH \cdot CH=CH \cdot CH_3)^+ \rightleftharpoons R_2 \cdot CH=CH \cdot CH=CH \cdot CH_3 + HX \] (5)

Step 3: Cyclization of a triene to form a substituted cyclohexadiene:
\[ R_2 \] (6)

Step 4: Formation of a tertiary carboxylation ion:
\[ R_1^+ + H_2C=CH \cdot CH=CH \cdot CH=CH \rightleftharpoons R_2 \] (7)

Step 5: Reaction of a tertiary carboxylation ion with Bronsted base to form substituted benzene:
\[ X^+ + H_2C=CH \cdot CH=CH \rightleftharpoons H_2C=CH \] (8)

Figure 2.5 Reaction mechanism for coke formation catalyzed by Bronsted acid sites [reprinted with permission from Elsevier, Copyright (2001)] [35].
2.5 Reaction kinetics

No previous studies were found related to the 4-methylstyrene hydrogenation or oligomerization kinetics. However, a few studies were found for similar model compounds, namely styrene and α-methylstyrene. Tables 2.2 and 2.3 report the catalysts used, reaction conditions, kinetic equations, and activation energies for styrene and α-methylstyrene hydrogenation reactions, respectively. Styrene hydrogenation activation energies were estimated to be 15-55, 27-31 and 61 kJ/mol over Pd(0.1-0.5 wt%), Rh(0.25-1 wt%) and Ni (5 wt%) catalysts, respectively. For α-methylstyrene hydrogenation, the activation energies were estimated to be 21-44 and 26-29 kJ/mol over Pd(0.5-5 wt%) and Rh(0.25-1 wt%) catalysts, respectively. At reaction conditions close to the current study, the activation energies were estimated to be 15 kJ/mol and 35 kJ/mol for styrene and α-methylstyrene hydrogenation reactions using Pd/Al₂O₃ catalyst, respectively.

Only one study reported the kinetics of α-methylstyrene dimerization over high-silica zeolite catalyst [42]. Although the study was performed at atmospheric pressure and relatively low temperature (60-100°C) with no H₂ present, it could shed some light on the dimerization reaction mechanism. A carbocation mechanism was proposed for the dimerization reaction forming 3 main dimers as shown in Figure 2.6. The activation energy was estimated to be 81, 76 and 99 kJ/mol for dimers 1, 2, and 3 formation, respectively.
Figure 2.6 Reaction mechanism for α-methylstyrene dimerization [reprinted with permission from Springer, Copyright (2012)] [42].
### Table 2.2 Styrene hydrogenation kinetics.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction condition</th>
<th>Kinetic equation</th>
<th>Activation energy (kJ/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 wt% Pd/Al₂O₃</td>
<td>60-180°C, 2.1-4.8MPa H₂</td>
<td>( r_{HYD} = k_{HYD} C_R ) (^a)</td>
<td>15</td>
<td>[43]</td>
</tr>
<tr>
<td>0.1 wt% Pd/C</td>
<td>15-45°C, constant H₂ pressure</td>
<td>( r_{HYD} = \frac{k_{HYD} C_R C_{H₂}}{(1 + K_2 C_R)^2} )</td>
<td>55</td>
<td>[44]</td>
</tr>
<tr>
<td>0.1 wt% Pd/SiO₂</td>
<td>18-60°C, 3.5MPa H₂</td>
<td>complex rate expression</td>
<td>23</td>
<td>[45]</td>
</tr>
<tr>
<td>0.3 wt% Pd/Al₂O₃</td>
<td>40-70°C, 2.0-5.0MPa H₂</td>
<td>( r_{HYD} = \frac{k_{HYD} C_R K_2 C_{H₂}}{A_1 A_2} )</td>
<td>31</td>
<td>[30]</td>
</tr>
<tr>
<td>0.5 wt% Pd/Al₂O₃</td>
<td>50-100°C, 0.6MPa (^d)</td>
<td>( r_{HYD} = \frac{k_{HYD} C_{H₂} C_{H₁}}{1 + K_{CPD} C_{CPD} + K_{HEX} C_{HEX}} )</td>
<td>54</td>
<td>[29]</td>
</tr>
<tr>
<td>0.25-1 wt% Rh/AlPO₄</td>
<td>20-50°C, 0.45-0.7MPa H₂</td>
<td>( r_{HYD} = k_{HYD} P_{H₂} )</td>
<td>27-31</td>
<td>[46]</td>
</tr>
<tr>
<td>5.4 wt% Ni/SiO₂</td>
<td>18-60°C, 3.5MPa H₂</td>
<td>complex rate expression</td>
<td>61</td>
<td>[45]</td>
</tr>
</tbody>
</table>

\(^a\) \( r_{HYD} \): hydrogenation rate expression; \( k_{HYD} \): hydrogenation rate constant; \( C_R \): model reactant concentration, mol/cm\(^3\).

\(^b\) when all phenyl acetylene is consumed. \( C_{H₂} \): dissolved H₂ concentration, mol/cm\(^3\); \( \rho_b \): catalyst bed density, g/cm\(^3\). \( K_2 \): Equilibrium constant of model reactant, cm\(^3\)/mol.

\(^c\) \( A_1 = 1 + \sqrt{K_{C_{H₂}}} \), where \( K_1 \) is equilibrium constant of H₂, cm\(^3\)/mol; \( A_2 = K_2 C_R + K_{CPD} C_{CPD} + K_{HEX} C_{HEX} \). \( K_{CPD} \) and \( K_{HEX} \) refer to equilibrium constant of cyclopentadiene and 1-hexene, respectively, cm\(^3\)/mol. \( C_{CPD} \) and \( C_{HEX} \) refer to cyclopentadiene and 1-hexene concentration, respectively, mol/cm\(^3\).

\(^d\) Temperature range is calculated based on the Arrhenius plot.

\(^e\) \( K_{th} \) is equilibrium constant of thiophene, cm\(^3\)/mol; \( C_{th} \) is thiophene concentration, mol/cm\(^3\).
Table 2.3 α-methylstyrene hydrogenation kinetics.

<table>
<thead>
<tr>
<th>Catalyst, wt%</th>
<th>Reaction condition</th>
<th>Kinetic equation</th>
<th>Activation energy (kJ/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-2.5 wt% Pd/Al₂O₃</td>
<td>10-35°C, 0.03-0.1 MPa H₂</td>
<td>( r_{HYD} = k_{HYD} P_{H₂}^{0.63} )</td>
<td>43</td>
<td>[47]</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>70-200°C</td>
<td></td>
<td>35</td>
<td>[48]</td>
</tr>
<tr>
<td>0.5-5 wt% Pd/Al₂O₃</td>
<td>25-110°C, 0.01-0.26 MPa H₂</td>
<td>( r_{HYD} = \frac{k_{HYD} K_2 C_R P_{H₂}}{1 + K_2 C_R} )</td>
<td>42</td>
<td>[49]</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>15-50°C, 0.1-1.5 MPa H₂</td>
<td>( r_{HYD} = \frac{k_{HYD} K_2 C_R P_{H₂}}{1 + K_2 C_R} )</td>
<td>39</td>
<td>[50]</td>
</tr>
<tr>
<td>0.5 wt% Pd/Al₂O₃</td>
<td></td>
<td></td>
<td>32</td>
<td>[51]</td>
</tr>
<tr>
<td>2 wt% Pd/Al₂O₃</td>
<td>27-40°C, 0.1 MPa H₂</td>
<td>( r_{HYD} = \frac{k_{HYD} K_2 C_R P_{H₂}}{1 + K_2 C_R} )</td>
<td>44</td>
<td>[52]</td>
</tr>
<tr>
<td>0.5 wt% Pd/Al₂O₃</td>
<td>32-52°C, 0.1 MPa H₂</td>
<td></td>
<td>21</td>
<td>[53]</td>
</tr>
<tr>
<td>1 wt% Pd/Al₂O₃</td>
<td>5-45°C, 0.1-0.6 MPa H₂</td>
<td>( r_{HYD} = \frac{k_{HYD} K_2 C_{H₂}}{(1 + K_1 C_{H₂})^2} )</td>
<td>39</td>
<td>[54]</td>
</tr>
<tr>
<td>0.25-1 wt% Rh/AlPO₄</td>
<td>20-50°C, 0.45-0.7 MPa H₂</td>
<td>( r_{HYD} = k_{HYD} P_{H₂} )</td>
<td>26-29</td>
<td>[46]</td>
</tr>
</tbody>
</table>

\( r_{HYD} \): hydrogenation rate expression; \( k_{HYD} \): hydrogenation rate constant; \( C_R \): model reactant concentration, mol/cm³; \( C_{H₂} \): dissolved H₂ concentration, mol/cm³.
2.6 Concluding remarks

- The molecular structure of the olefin/diolefin (conjugated/non-conjugated, cyclic/linear, olefin, steric hindrance effect) plays an important role in determining the hydrogenation and isomerization activity and selectivity. This was confirmed for isoprene reacted over MoS$_2$ and MoS$_2$/γ-Al$_2$O$_3$ catalysts. However, no previous studies examined how olefin/diolefin molecular structure might possibly affect dimerization/oligomerization reactions.

- Although it was confirmed that the rate of conjugated olefin/diolefin hydrogenation is always faster than that of mono-olefin hydrogenation, experiments with the addition of mono-olefin were performed to account for other roles that the mono-olefin might play in dimerization/oligomerization reactions, catalyst deactivation and reactor fouling.

- H$_2$S dissociative adsorption on Ni-Mo-S/γ-Al$_2$O$_3$ can convert a sulphur vacancy to a -SH group and a Bronsted acid site. In addition, P$_2$O$_5$ promoter can be a source of Bronsted acid sites. The reaction of the olefin/diolefin with a Bronsted acid leads to the formation of a carbocation, the intermediate required for dimerization reactions. The support acidity can play a role in initiating oligomerization reactions as oligomers were detected with increasing support acidity under mild hydrotreating conditions (250°C and 17 MPa).

- Olefin, diolefin and aromatics can oligomerize to produce coke over acidic catalytic sites. The reactions involve formation of an intermediate carbocation by reaction with a Bronsted acid or a primary carbocation, dimerization/oligomerization by reacting with other olefins, diolefins or aromatics and finally termination by reaction with a Bronsted base. This is the
main catalyst deactivation mechanism and may also be responsible for reactor fouling. In this study, the link between olefin/diolefin dimerization, catalyst deactivation and reactor fouling will be examined.

- Previous studies reported styrene hydrogenation activation energies of 15-55, 27-31 and 61 kJ/mol over Pd(0.1-0.5 wt%), Rh(0.25-1 wt%) and Ni (5 wt%) catalysts, respectively. For α-methylstyrene hydrogenation, activation energies of 21-44 and 26-29 kJ/mol over Pd(0.5-5 wt%) and Rh(0.25-1 wt%) catalysts were reported, respectively. One study reported activation energy ranging from 76-99 kJ/mol for α-methylstyrene dimerization over high-silica zeolite catalyst at atmospheric pressure and relatively low temperature (60-100°C) with no H₂ present. No studies investigated hydrogenation and dimerization kinetics for 4-methylstyrene over commercial Ni-Mo-S/\(\gamma\)-Al₂O₃ catalyst at industrially relevant reaction conditions (< 250°C temperature, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and a constant H₂/feed ratio of 392 standard mL/mL).

- No studies were found that report the effect of temperature and olefin/diolefin content on hydrogenation and dimerization activity over commercial Ni-Mo-S/\(\gamma\)-Al₂O₃ catalyst at industrially relevant reaction conditions (< 250°C temperature, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and a constant H₂/feed ratio of 392 standard mL/mL).
Chapter 3: Experimental

This chapter explains the detailed experimental methods that were utilized in this study. In the first part, the reaction and analytical supplies used including model compounds, catalysts, and gases are described. This is followed by a description of the analytical techniques used to characterize the catalyst. Finally, an explanation of the catalyst activity measurement is given.

3.1 Reaction and analytical supplies

3.1.1 Model compounds

The model compounds used in this study, their structures, purities and suppliers are summarized in Table 3.1.

3.1.2 Hydrotreated light gas oil (HTGO)

In some experiments, HTGO, from Syncrude, was used as a solvent. The properties of the HTGO are listed in Table 3.2.
Table 3.1 The structure, purity and supplier of model compounds used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-dimethyl-2,4-hexadiene</td>
<td><img src="structure1.png" alt="Structure" /></td>
<td>96%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Isoprene</td>
<td><img src="structure2.png" alt="Structure" /></td>
<td>≥99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td><img src="structure3.png" alt="Structure" /></td>
<td>96%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>1,4-cyclohexadiene</td>
<td><img src="structure4.png" alt="Structure" /></td>
<td>97%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>2,4-hexadiene</td>
<td><img src="structure5.png" alt="Structure" /></td>
<td>90%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>1,3-pentadiene</td>
<td><img src="structure6.png" alt="Structure" /></td>
<td>90%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>1,4-pentadiene</td>
<td><img src="structure7.png" alt="Structure" /></td>
<td>99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>1,3-cyclooctadiene</td>
<td><img src="structure8.png" alt="Structure" /></td>
<td>98%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1,5-cyclooctadiene</td>
<td><img src="structure9.png" alt="Structure" /></td>
<td>≥99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>α-terpinene</td>
<td><img src="structure10.png" alt="Structure" /></td>
<td>≥90%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>4-vinyl-cyclohexene</td>
<td><img src="structure11.png" alt="Structure" /></td>
<td>99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Styrene</td>
<td><img src="structure12.png" alt="Structure" /></td>
<td>99%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>4-methylstyrene</td>
<td><img src="structure13.png" alt="Structure" /></td>
<td>≥98%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>α-methylstyrene</td>
<td><img src="structure14.png" alt="Structure" /></td>
<td>99%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>1-octene</td>
<td><img src="structure15.png" alt="Structure" /></td>
<td>≥99%</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td><img src="structure16.png" alt="Structure" /></td>
<td>99%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Decalin</td>
<td><img src="structure17.png" alt="Structure" /></td>
<td>98% cis+trans</td>
<td>Alfa Aesar</td>
</tr>
</tbody>
</table>
Table 3.2 Syncrude HTGO product properties [55].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling range</td>
<td>°C</td>
<td>177-343</td>
</tr>
<tr>
<td>Gravity</td>
<td>°API</td>
<td>36.2</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>wppm</td>
<td>65</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>wppm</td>
<td>25</td>
</tr>
<tr>
<td>Aromatics content</td>
<td>wt%</td>
<td>20</td>
</tr>
<tr>
<td>Cetane number</td>
<td>-</td>
<td>40</td>
</tr>
</tbody>
</table>

3.1.3 Catalyst

The catalyst used in this study was a Criterion 424 hydrotreating catalyst. The fresh catalyst composition is summarized in Table 3.3 as reported by the manufacturer. Initially, fresh catalyst in oxide form was pre-sulphided before use. However, because of the high activity of the fresh catalyst, the oligomerization reactions, catalyst deactivation and reactor fouling were examined using a spent catalyst in sulphide form, recovered from a Syncrude naphtha hydrotreater after shutdown. The fresh and spent catalyst elemental compositions are shown in Table 3.4. The fresh catalyst composition was calculated from the values reported in Table 3.3. The spent catalyst elemental analysis for Al, Ni, Mo, P, C and S was completed by the Canadian Microanalytical Services Inc. in Delta, BC, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in accordance with the US EPA 6010C method.
Table 3.3 Criterion 424 hydrotreating catalyst composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>60-85</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>15-25</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>NiO</td>
<td>1-6</td>
</tr>
</tbody>
</table>

Table 3.4 Spent Criterion 424 hydrotreating catalyst elemental composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
</tr>
<tr>
<td>Al</td>
<td>31.76-44.9</td>
</tr>
<tr>
<td>Ni</td>
<td>0.79-4.71</td>
</tr>
<tr>
<td>Mo</td>
<td>10.00-16.66</td>
</tr>
<tr>
<td>P</td>
<td>0-4.36</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
</tr>
</tbody>
</table>

3.1.4 Gases

Ultra-high purity helium (He, Praxair, UHP 5.0, 99.999%) and hydrogen (H$_2$, Praxair, UHP 5.0, 99.999%) were used throughout this study.
3.2 Catalyst characterization

In order to relate catalyst properties to the onset and rate of catalyst deactivation and reactor fouling, several analytical techniques were used to characterize both the fresh and the used catalysts.

The total BET surface area, pore volume, and average pore width of the sulfide catalysts were analyzed by N\textsubscript{2} adsorption using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry instrument. The catalyst sample was placed in a special glass tube, degassed at 1.33 kPa/s and heated at a ramp rate of 10°C/min until 0.04 kPa and 250°C. The temperature was then held at 250°C for 240 min. Subsequently the cooled sample was analyzed using N\textsubscript{2} adsorption. The equations used for the calculation of the total BET surface area are included in Appendix B.

In addition, the carbon, hydrogen, nitrogen and sulphur contents of the catalysts were determined by elemental CHNS analysis using a Perkin-Elmer 2400 Series II CHNS/O analyzer.

The aluminum, molybdenum, phosphate and nickel contents of the catalyst was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in accordance with the US EPA 6010C method. The analysis was performed by the Canadian Microanalytical Service Ltd. in Delta, BC.

The repeatability of the catalyst characterization is discussed in Appendix C.
3.3 Catalyst activity measurement

3.3.1 Reaction system

The reactions were performed in a micro-scale fixed bed reactor (length 50 cm; hot zone 30 cm) with an internal diameter of 1.18 cm. The catalyst volume ranged from 0.625-5 mL (0.5-4 g). The feed consisted of 2-20 wt% olefin/diolefin in a solvent (decalin or HTGO). The operating conditions ranged from 150-250°C temperature, 3-4 MPa H₂ total pressure, 1-8 hr⁻¹ LHSV, and a constant H₂/feed ratio of 392-1200 standard mL/mL. These operating conditions include and expand Syncrude commercial operating conditions [56]. A schematic diagram of the reactor system is shown in Figure 3.1. As shown in the figure, the liquid feed was mixed with the gas and the mixture entered the reactor from the top. The reactor was operated in a trickle bed mode with three phases: the liquid feed and H₂ gas mixture flowing downward over the solid catalyst bed. The reaction took place in the reactor over the catalyst and the product mixture flowed from the bottom of the reactor to the ambient temperature condenser where the liquid accumulated. The liquid product was collected every 24 hours and analyzed. The gas from the condenser flowed through a scrubber containing NaOH (1 M) to remove any H₂S. Part of the gas flowed to the Gas Chromatograph (GC) for analysis and the rest was vented.

In terms of process control and instrumentation, the liquid flow was controlled using a Shimadzu LC-20AD parallel type double plunger pump. The inlet gas flow was controlled using Brooks SLA5850 Thermal Mass Flow Controllers with a Brooks Model 0260 personal computer (PC) interface software. The system pressure was controlled using a manual back pressure regulator (Tescom 26-1765-24-098). The catalyst bed temperature was controlled by Lindberg/Blue M
Mini-Mite Tube Furnace and an OMEGA K-type thermocouple inserted in the middle of the catalyst bed interfaced to a SpecView PC interface software. The reactor pressure was monitored by a pressure gauge and an Omega PX409 USB pressure transducer. The differential pressure across the reactor was measured every minute by an Omega PX80 Industrial Wet/Wet Differential Pressure Transmitter. The outlet gas flow was monitored using a Brooks SLA5860 Thermal Mass Flow Meter with a Brooks Model 0260 PC interface software.

The inlet and outlet gas flows, system pressure, differential pressure across the reactor, and the catalyst bed temperature were all monitored and recorded using a PC. In addition, a scale placed under the feed flask was used to monitor the mass of the liquid feed in order to measure the mass of the liquid in, compared to the mass of the product liquid, and hence calculate the overall mass balance. For all the experimental tests reported, the mass balance was > 92%.
Figure 3.1 A schematic diagram of the micro-scale fixed bed reactor system.
3.3.2 Safety considerations

To avoid flammable gas accumulation and toxic gas exposure, the reaction system was built in a vented plexiglass cage with a hinged front door for entrance. A Draeger Pac 5500 H₂S gas detector (range 0-100 ppm) was placed inside the cage to detect leaked H₂S gas. In addition, the floor inside the cage was covered with a Rubber Flat Rib Antislip Traction mat to prevent slipping and contain chemical spills. To avoid excessive pressure build up, a high pressure Swagelok proportional relief valve model R3A set at 6.2 MPa was installed on the gas inlet line. To avoid overheating, the reactor temperature control system was equipped with two adjustable alarm set points. When the first alarm set point was reached, a warning was displayed. When the second set point was reached, the heating automatically shut off until the temperature was reduced to below the set point.

In addition, a main emergency shut-off switch was also installed inside the cage to manually shutdown the reactor system instruments in case of emergency.

3.3.3 Catalyst loading

The reactor was loaded as shown in Figure 3.2. Starting from the bottom, the reactor was loaded with 11.8 cm of 3 mm glass beads followed by 3.5, 1.4 and 1.4 cm silicon carbide (SiC) mesh sizes #16, #46 and #80, respectively. This was followed by the catalyst bed consisting of 4.6 cm of mesh size #80 SiC and 2 g of catalyst. The SiC and the catalyst were divided equally into 2 parts and loaded one after another. The top of the catalyst bed was loaded with 1.1 cm of each SiC mesh size #80, #46 and #16 followed by 14.8 cm of 3 mm glass beads. This catalyst loading
was recommended by several studies for naphtha and gas oil hydrotreating in micro-reactor systems with 10-12 mm internal diameter and 2-3 mm trilobe commercial catalyst [57-61]. Previous studies reported that this catalyst loading technique eliminated poor catalyst wetting, wall effect and backmixing in micro-reactor systems and the data produced were more reliable and in agreement with bench scale and commercial reactor systems [61]. The detailed calculations of the catalyst overall effectiveness factor, axial dispersion and wall effects are included in Appendix D. Although the ratio of bed height to equivalent pellet diameter, $L_b/d_e$, and the ratio of reactor diameter to equivalent pellet diameter, $d_r/d_e$, are much larger for a commercial reactor than the micro-scale reactor used in this study, the ratios were found to be larger than 30 and 4, respectively, for the micro-scale reactor, satisfying the rule of thumbs for negligible axial mass dispersion [62, 63] and wall effects [62-64]. Although other reports suggest a $d_r/d_e$ ratio > 10 [65, 66] and > 16 [67] to minimize wall effects, direct measurements reported for a very similar reaction system [57-61] suggests that the dimensions of the current system provide ideal reactor hydrodynamics for the experiments of this study.

3.3.4 Reactor system operation

Prior to starting up the reactor system, a leak test was performed to ensure no leaks were present. The leaks were detected using a Restek electronic leak detector. Once the system preserved a pressure of ~4 MPa for at least 24 hours, the experimental run was started.
3.3.4.1 Reactor startup with oxide catalyst

In order to obtain the optimal activity, the commercial catalyst must be transformed from the oxide state to the sulphide state inside the micro-scale fixed bed reactor. This was achieved following standard procedures provided by the catalyst developer and modified by several studies for micro-scale reactors as follows [57, 58, 60, 61, 68-70]:

Figure 3.2 A schematic diagram of reactor bed loading.
1. The reactor was pressurized with He to the desired experimental pressure by setting the gas flow to 500 standard mL/min.

2. He flow was adjusted to 50 standard mL/min and the reactor temperature was raised to 100°C at 5°C/min.

3. At 100°C, the catalyst wetting was commenced with 3 vol% butanethiol in gas at 2.5 mL/min for 1 h. The liquid flow was then adjusted to 5 mL/h (LHSV of 1 h⁻¹). He flow was stopped and H₂ flow was started at 600 standard mL/mL feed.

4. The reactor temperature was raised from 100 to 193°C and maintained for 24 h.

5. The reactor temperature was adjusted to the desired reaction temperature and left for 24 h.

6. The feed was switched to the desired feed and the liquid feed flow was started at 5 mL/h.

The calculation of the minimum amount of butanethiol needed to presulphide the catalyst is included in Appendix E.

3.3.4.2 Reactor start-up with presulphided catalyst

When the presulphided spent catalyst, recovered from a Syncrude naphtha hydrotreater after shutdown, was used, the standard startup procedure was as follows:

1. The reactor was pressurized with He to the desired experimental pressure by setting the gas flow to 500 standard mL/min.

2. He flow was adjusted to the desired H₂/feed ratio and the reactor temperature was raised to desired reaction temperature at 5°C/min.
3. Once the desired reaction temperature was reached, the reactor was depressurized to ambient pressure, and the He or N₂ flow was stopped.

4. The reactor was then pressurized with H₂ to the desired reaction pressure.

5. Once the reaction pressure was reached, the H₂ flow was adjusted to the desired H₂/feed ratio and the liquid feed flow was started at 5 mL/h.

3.3.4.3 Reactor shutdown

When the experimental run was completed, the reactor was shut down using the procedure as follows:

1. The liquid feed flow was stopped.
2. The furnace was turned off.
3. H₂ flow was stopped and He flow started at 32.7 standard mL/min.
4. Once ambient temperature was reached, the reactor was depressurized to ambient pressure.

3.3.5 Liquid sample analysis

The liquid samples were collected every 24 h and characterized using several techniques as follows: gas chromatography mass spectrometry (GC-MS), gum content by jet evaporation (ASTM D381-12), olefin content by fluorescent indicator adsorption (ASTM D1319-10), bromine number/olefin content by electrometric titration (ASTM D1159-07), diene value by
maleic anhydride addition reaction (UOP 326-08) and carbon-13 nuclear magnetic resonance ($^{13}$C NMR). The repeatability of the liquid analysis is discussed in Appendix C.

3.3.5.1 Gas chromatography mass spectrometry (GC-MS)

A Shimadzu QP-2010S Gas Chromatograph-Mass Spectrometry (GC-MS) equipped with a Shimadzu RXI-5MS column (ID 0.25 mm, length 30 m, film 0.25 μm) and AOC-20i autosampler (10 μL syringe) was used in order to identify and quantify the components. The unknown components were identified using a similarity search implemented in Shimadzu’s GCMSsolution (Version 2.50). The similarity search compares the spectrum of the unknown component to the standard mass spectra in NIST/EPA/NIH Mass Spectral Library (NIST 05) database library. The components with the most similar mass spectra are then listed in order, based on the degree of similarity (similarity index). Peak assignment was based on the compounds identified with the highest similarity index. Prior to analysis, the liquid samples were diluted in decalin to prevent column overloading/detector saturation. The GC-MS was calibrated using different analytical standards that reflect the model compounds used and the major products of reaction (refer to Appendix F for details). From the GC-MS results, the conversion ($X$), selectivity ($S$), and yield ($Y$) was calculated as follows:

\[
A \xrightarrow{\text{A}} B + C
\]

\[
X_A = 1 - \frac{C_{W(A)}}{C_{W(A0)}} = \frac{C_{W(B)} + C_{W(C)}}{C_{W(A)} + C_{W(B)} + C_{W(C)}}
\]
\[ S_B = \frac{C_{W(B)}}{C_{W(B)} + C_{W(C)}} \]

\[ Y_B = \frac{C_{W(B)}}{C_{W(A)} + C_{W(B)} + C_{W(C)}} \]

where,

\( C_{W(j)} \) = weight fraction of component j, wt%.

\( C_{W(j0)} \) = feed weight fraction of component j, wt%.

Figure 3.3 illustrates the difference between the conversion, selectivity and yield.
The reactant conversion at a fixed set of operating conditions was used as a measure of relative activity of the catalyst for the various olefin/diolefin reactants investigated in the current study.

### 3.3.5.2 Gum content by jet evaporation (ASTM D381-12 [71])

This test method is used to determine the gum content in aviation fuels, motor gasolines or other volatile distillates. In this study, the method was used to quantify the gum content in the liquid sample and relate it to oligomer content, catalyst deactivation and reactor fouling. The instrument used to perform the analysis was an Anton Paar Gum Content Tester. To determine the amount of gum in the sample, approximately 50 mL of the liquid product sample was evaporated for 30 min under controlled temperature (232°C well temperature) and steam flow (1000 standard mL/s). The residue was then weighed and the result was expressed as mg gum per 100 mL sample.

### 3.3.5.3 Bromine number/olefin content by electrometric titration (ASTM D1159-07 [72])

Defined as the number of grams of Br2 that reacts with 100 g of product, the bromine number gives an empirical measurement of the degree of aliphatic unsaturation in the tested sample. The test is based on the following reaction:

![Chemical Reaction Diagram]

\[ RC\equiv CR' \xrightarrow{Br_2} RC-\cdot CR' \]
Before measuring the bromine number, 1 L of titration solvent was prepared by mixing 714 mL glacial acetic acid, 134 mL dichloromethane, 134 mL methanol and 18 mL diluted sulphuric acid (1:5 H₂SO₄: H₂O volume). The bromide-bromate titration solution (0.25 M as Br₂) was prepared by dissolving 51 g of potassium bromide and 13.92 g of potassium bromate, both dried at 105°C, in water to give a total volume of 1 L.

The sample solution was prepared by dissolving 0.6-20 g of sample in dichloromethane to give a total volume of 50 mL. After that, 110 mL of the titration solvent and 5 mL of the sample solution were added to the titration vessel. The contents of the titration vessel were maintained at 4.5°C during the titration by cooling the jacketed glass vessel and continuous stirring using a magnetic stirrer. The mixture was titrated with standard bromide-bromate solution using QC-Titrate (PCM-QSAB/A) electrometric titration system. A sudden change in potential due to free bromine when all double bonds are saturated determined the end point on the electrometric end point titration apparatus. The test was repeated in the same manner using 5 mL of dichloromethane instead of the sample solution. Based on the results, the bromine number was calculated according to the following equation:

\[
\text{Bromine number} = \frac{(A_{BN} - B_{BN})(M_{BN})(15.98)}{W_{BN}}
\]

where,

\[A_{BN} = \text{bromide-bromate solution titration volume for the sample, mL.}\]

\[B_{BN} = \text{bromide-bromate solution titration volume for the blank, mL.}\]
\( M_{BN} \) = bromide-bromate solution molarity, M.

15.98 = conversion factor.

\( w_{BN} \) = weight of sample in the aliquot, g.

### 3.3.5.4 Diene value by maleic anhydride addition reaction (UOP 326-08 [73])

Diene value is defined as the weight of iodine, in g, equivalent to the maleic anhydride amount that can react with 100 g of the test sample (basis: 2 iodine atoms per one mole of maleic anhydride). This method determines the reactivity of maleic anhydride (Diels-Alder) with different oils. From the results, an empirical measure of conjugated diolefin in the sample can be determined. An example of the Diels-Alder butadiene reaction with maleic anhydride is shown in following equation [74]:

\[
\begin{align*}
\text{\( \text{C}_{2}\text{H}_{4} \) + \( \text{C}_{4}\text{H}_{6}\text{O}_{3} \) & \xrightarrow{100^\circ\text{C}} \text{\( \text{C}_{12}\text{H}_{10}\text{O}_{4} \) } \\
\text{benzene} & \end{align*}
\]

Initially, maleic anhydride solution was prepared by mixing 60 g maleic anhydride with warm toluene and then cooling and diluting to achieve a total volume of 1 L. After one day, the solution was filtered using a filter paper (qualitative grade). Then about 10 g of the sample and 20 mL of the filtered maleic anhydride solution were refluxed for 3 hours and then cooled to ambient temperature. After cooling, 5 mL of water was added to the mixture and boiled for 15 minutes and then cooled to ambient temperature. After cooling, 5 mL methyl-tertiary butylether
(MTBE) followed by 20 mL water were added to the mixture through the top of the condenser. The mixture was transferred to a separatory funnel and the aqueous layer was extracted after shaking for 4-5 minutes, venting occasionally. The extraction was repeated three times in the same manner by adding 25, 10 and 10 mL of water, respectively. The extracted aqueous layer was then titrated with 1 M NaOH using a QC-Titrator (PCM-QSAB) potentiometric titration system. A blank was prepared and titrated in the same manner, excluding the sample addition. The net volume obtained by potentiometric titration difference was considered the amount reacted with the sample. From these results, the diene value can be obtained using the following equation:

\[
\text{Diene value} = \frac{(B_{DV} - A_{DV})(M_{DV})(12.69)}{W_{DV}}
\]

where,

\(A_{DV}\) = sodium hydroxide solution titration volume for the test, mL.

\(B_{DV}\) = sodium hydroxide solution titration volume for the blank, mL.

\(M_{DV}\) = sodium hydroxide solution molarity, M.

12.69 = conversion factor.

\(W_{DV}\) = weight of the diene value sample, g.
3.3.5.5 **Olefin content by fluorescent indicator adsorption (ASTM D1319-10 [75])**

This method determines the content of aromatics, olefins, and saturates in petroleum fractions with boiling point lower than 315°C. All results reported for this method were performed by CanmetENERGY, Natural Resources Canada located in Devon, Alberta.

About 0.75 mL of sample was injected to adsorb into a special glass adsorption column filled with silica gel, a small layer of which contains fluorescent dyes. Alcohol was then added to desorb the sample and the aromatics, olefins and saturates were separated based on their adsorption affinities with the dyes on the boundaries. The zones were visible under ultraviolet light and the length of each zone was determined. From the length, the volume of content of the aromatics, olefins, and saturates was calculated.

3.3.5.6 **Carbon-13 nuclear magnetic resonance (\(^{13}\)C NMR)**

\(^{13}\)C NMR analysis was performed on selected liquid products and gum samples to determine the different carbon functional groups in different environments in order to confirm the structures of the dimers. The \(^{13}\)C NMR analysis sample was prepared by diluting the liquid product or gum sample with at least 20 wt% dichloromethane-d2 (CD\(_2\)Cl\(_2\)). The analysis was completed by The Nuclear Magnetic Resonance facility, Department of Chemistry, University of British Columbia in Vancouver, BC. The instrument used was a Bruker Avance 400dir Spectrometer.
3.3.6 Gas product analysis

The gas product samples were analyzed periodically using a Shimadzu GC-14B, equipped with an Agilent HP-PLOT U column (ID 0.530 mm, length 30 m, film 20.00 μm) and a flame ionization detector (FID). The results indicated very low amounts of cracked products in the gas phase. Therefore, the products present in the gas phase were ignored in the following discussions.
Chapter 4: Determining the onset of oligomer formation

In this chapter, the preliminary experiments completed to determine the onset of olefin/diolefin oligomerization are discussed. The aim of these experiments was to investigate the process conditions that lead to oligomer formation. As discussed earlier in Chapter 2, conjugated olefins/diolefins can form allylic carbocations, the intermediate required for dimer/oligomer formation. Therefore, conjugated diolefins, namely 2,5-dimethyl-2,4-hexadiene and isoprene, were selected as model diolefins in the current investigation diluted in either decalin or HTGO. The process conditions were varied to examine the effect on hydrogenation and oligomerization.

4.1 Fresh sulphided Ni-Mo-S/γ-Al₂O₃ tests

Initially, 17.8 wt% 2,5-dimethyl-2,4-hexadiene was added to decalin and hydrogenated over fresh sulphided Ni-Mo-S catalyst supported on γ-Al₂O₃ (Criterion 424 hydrotreating catalyst). Prior to reaction, the catalyst was presulphided as discussed in Section 3.3.4.1. The reaction was operated over a temperature range of 150-250°C, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and 600 standard mL/mL H₂/feed ratio. Toward the end of the run, the solvent was switched from decalin to HTGO supplied by Syncrude, in order to see if HTGO components enhance oligomerization and to better mimic industrial conditions. The hydrogenation was carried out at T=230-250°C with other conditions fixed (P=3.4 MPa, LHSV=2hr⁻¹, H₂/feed ratio=600 standard mL/mL). The experiments were performed sequentially on the same catalyst bed for a total of 35 days TOS. Each set of process conditions was maintained for 5 days TOS.
The results with 2,5-dimethyl-2,4-hexadiene in decalin as the feed are summarized in Table 4.1. From Table 4.1, the conversion was relatively low at 150°C with 45.4 ± 0.6 % of 2,5-dimethyl-2,4-hexadiene converted mostly to the partially hydrogenated product 2,5-dimethylhexene with approximately 97.4 ± 0.8 wt% selectivity. At ≥ 180°C, the conversion reached 100 ± 0 % with the diolefin converted mostly to 2,5-dimethylhexane with 97.2 ± 0.7 wt% selectivity at 180°C and 100 ± 0 wt% selectivity at ≥ 200°C. No oligomer formation or reactor fouling was detected at these operating conditions as determined from the GC-MS results and the constant low pressure drop across the reactor, shown in Figure 4.1, respectively.

Table 4.1 Product yield versus temperature (Feed: 17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2h⁻¹, H₂/feed ratio=600 standard mL/mL, catalyst: fresh sulphided Ni-Mo-S/γ-Al₂O₃ - Criterion 424).

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>150</th>
<th>180</th>
<th>200</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOS, h</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Cumulative TOS, h</td>
<td>360</td>
<td>600</td>
<td>720</td>
<td>840</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-dimethylhexane</td>
</tr>
<tr>
<td>2,5-dimethylhexene</td>
</tr>
<tr>
<td>Conversion, %</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 4 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
Figure 4.1 Measured pressure drop across reactor (Feed: 17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin or HTGO, T=150-250°C, P=3.4 MPa, LHSV=2h⁻¹, H₂/feed ratio=600 standard mL/mL, catalyst: fresh sulphided Ni-Mo-S/γ-Al₂O₃ - Criterion 424).

After 35 days TOS, the solvent was switched from decalin to HTGO. The hydrogenation was carried out at T=230-250°C with other conditions fixed as before (P=3.4 MPa, LHSV=2h⁻¹, H₂/feed ratio=600 standard mL/mL) for up to 49 days TOS total. The reaction at 250°C was performed for 9 days then the temperature was reduced to 230°C and maintained for 5 more days. The product yields could not be obtained by GC-MS as the HTGO peaks and the product peaks overlapped. Therefore, bromine number and diene value tests were performed on the samples and the results are summarized in Table 4.2. The data of Table 4.2 show that the
bromine number decreased when the feed was converted indicating a high degree of hydrogenation. This was also confirmed by analysis of the hydrocarbon type using fluorescent indicator adsorption (FIA) analysis as the results showed a significant decrease in aromatics content from 85.9 vol% to 41.9-42.7 vol% and an increase in saturates from 14.1 vol % to 57.3-58.1 vol% after reaction. The bromine number obtained at 230°C was slightly higher than that at 250°C indicating a slightly lower hydrogenation activity. The diene value however was unchanged between the feed and the product indicating that the test was not suitable for measuring the conjugated diolefin content for 2,5-dimethyl-2,4-hexadiene as the methyl groups attached to the double bonds might sterically hinder reactivity with maleic anhydride and therefore prevent diene value determination. Again, no oligomer or reactor fouling was detected at these operating conditions based on the bromine number and diene value results or the pressure drop across the reactor shown in Figure 4.1, respectively. Gum content tests were completed on both the feed and product but the gum results were not appropriate as the test resulted in large quantities of liquid instead of gum (>18000 mg/100 mL). These results show that it is difficult to determine oligomer formation and link it to gum formation and reactor fouling when HTGO is used as a solvent.
Table 4.2 Bromine number, diene value, gum content, and hydrocarbon type by fluorescent indicator adsorption (FIA) versus temperature (Feed: 17.8 wt% 2,5-dimethyl-2,4-hexadiene in HTGO, T=230-250°C, P=3.4 MPa, LHSV=2h⁻¹, H₂/feed ratio=600 standard mL/mL, catalyst: fresh sulphided Ni-Mo-S/γ-Al₂O₃ - Criterion 424).

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOS, h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cumulative TOS, h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromine number, g/100 g</td>
<td>41.0*</td>
<td>5.1 ± 0.1**</td>
</tr>
<tr>
<td>Diene value, g I₂/100 g</td>
<td>1.0 ± 0.1</td>
<td>0.3 ± 0.3</td>
</tr>
<tr>
<td>Hydrocarbon type by FIA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics, vol%</td>
<td>85.9</td>
<td>41.9</td>
</tr>
<tr>
<td>Olefins, vol%</td>
<td>&lt; 0.3</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>Saturates, vol%</td>
<td>14.1</td>
<td>58.1</td>
</tr>
</tbody>
</table>

*Theoretical value calculated based on diolefin content.
**Standard error.

4.2 Spent sulphided Ni-Mo-S/γ-Al₂O₃ tests

In order to determine if catalyst activity is linked to oligomer formation, spent Ni-Mo-S catalyst supported on γ-Al₂O₃ (Criterion 424, spent), recovered from a Syncrude naphtha hydrotreater after shutdown, was tested. All of the experiments reported in this section were performed sequentially on the same catalyst bed. Each set of reaction conditions was held for 5-7 days as indicated. Similar to the fresh catalyst tests, 17.8 wt% 2,5-dimensional-2,4-hexadiene in decalin was
hydrogenated over a temperature range of 180-200°C, 3.4 MPa H₂ pressure, 2 hr⁻¹ LHSV, and 600 standard mL/mL H₂/feed ratio. Additional tests at LHSV of 1 hr⁻¹, and H₂/feed ratio of 300 standard mL/mL were performed at T=180°C to investigate the effect of LHSV and H₂/feed ratio on the reactions, respectively. Subsequently the feed was changed to 5 wt% 2,5-dimethyl-2,4-hexadiene + 20 wt % 1-octene in decalin to better mimic the industrial feed in terms of olefin and diolefin content. The new reactions were completed at 180-250°C, LHSV of 2h⁻¹ and H₂/feed ratio of 392 standard mL/mL; process conditions relevant to industrial olefin/diolefin saturation hydrotreaters. One test was performed using a He/feed ratio of 392 standard mL/mL with no H₂ to determine if oligomerization is linked to a lack of H₂. The results are summarized in Table 4.3. For the first time, oligomers were detected in the product. However, due to the small amounts (≤1.2wt% yield), it was not possible to identify the oligomer structures using GC-MS and no clear trend between the oligomer content and the reaction conditions could be established. The low oligomerization activity is most likely related to the steric hindrance created by the methyl group attached to each double bond. The methyl groups limit access and reactivity of the double bonds and therefore less oligomerization activity is obtained. In addition, the pressure drop data, shown in Figure 4.2, did not indicate any form of reactor fouling. When He was used instead of H₂, the conversion was low (< 8%) with low oligomerization activity (0.1 wt%) and therefore no link can be drawn between the lack of H₂ and oligomerization.
Table 4.3 Product yield versus temperature (Feed: 17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin or 5 wt% 2,5-dimethyl-2,4-hexadiene + 20 wt % 1-octene in decalin, P=3.4 MPa, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>T, °C</th>
<th>17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin</th>
<th>5 wt% 2,5-dimethyl-2,4-hexadiene + 20 wt % 1-octene in decalin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>180 180 200 180</td>
<td>180 250 250</td>
</tr>
<tr>
<td>LHSV, hr⁻¹</td>
<td>1 2 2 2</td>
<td>2 2 2</td>
</tr>
<tr>
<td>H₂/Feed, standard mL/mL</td>
<td>600 600 600 300</td>
<td>392 392 392 (He)</td>
</tr>
<tr>
<td>TOS, h</td>
<td>144 120 168 120</td>
<td>120 120 120</td>
</tr>
<tr>
<td>Cumulative TOS, h</td>
<td>144 264 432 552</td>
<td>672 792 912</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-dimethyl-2,4-hexadiene isomers</td>
</tr>
<tr>
<td>2,5-dimethyl-hexene</td>
</tr>
<tr>
<td>2,5-dimethyl-hexane</td>
</tr>
<tr>
<td>Oligomers</td>
</tr>
<tr>
<td>Other</td>
</tr>
<tr>
<td>Conversion, %</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from consecutive days TOS on the same catalyst bed at the same process conditions.
Figure 4.2 Measured pressure drop across reactor (Feed: 17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin or 5 wt% 2,5-dimethyl-2,4-hexadiene + 20 wt % 1-octene in decalin, P=3.4 MPa, catalyst: spent Ni-Mo-S/γ-Al2O3).

Using the same catalyst bed, the feed was switched to 17.8 wt% isoprene in decalin. Based on previous studies discussed in Chapter 2, steric hindrance effects of the methyl group attached to the double bond weakens the adsorption of the double bond to the catalyst and therefore reduces the reactivity. 2,5-dimethyl-2,4-hexadiene has a methyl group attached to each double bond giving it higher steric hindrance compared to isoprene, which has a methyl group attached to only one double bond. When the feed was changed to isoprene, large quantities of oligomers were formed as shown in Figure 4.3. The selectivity to oligomers reached more than 80 wt%, whereas the hydrogenation activity diminished to less than 20 wt% total hydrogenated products formed. Moreover, after less than three days of operation, the conversion decreased sharply to
52.1% (TOS=1100 h) from 98.4% in the second day (TOS=1080 h) indicating significant catalyst activity loss. Furthermore, the pressure drop increased sharply as shown in Figure 4.4 and the reactor plugged forcing reactor shutdown. Note that 17.8 wt% isoprene in decalin reflects a diene value of 66.3 g I₂ / 100 g, about 7 times the reported diene value of the industrial naphtha feed.

![Figure 4.3 Product selectivity versus TOS (17.8 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).](image_url)
Figure 4.4 Measured pressure drop across reactor (17.8 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

The catalyst was analyzed before and after reaction (TOS=1100 h⁻¹) and the results are listed in Tables 4.4 and 4.5. Note that the results reflect the cumulative catalyst deactivation and carbon deposition from all the operating conditions discussed in this section as the reactions were performed sequentially on the same catalyst bed. Therefore, it's not possible to directly link the reaction activity at a set of process conditions to the catalyst properties. This relationship is investigated in Chapter 7 where the catalyst was analyzed after reaction at a fixed set of operating conditions. The results of Table 4.4 and 4.5 illustrate that there was a significant decrease in surface area, pore volume and pore size while the carbon content increased. This can be explained by the deposition of oligomers in the catalyst pores covering active sites and
blocking access to catalyst pores, hence the decrease in catalyst activity that was noticed toward the end of the run. The oligomer formation and deposition in the catalyst bed eventually led to reactor fouling as indicated by the sharp increase in pressure drop in Figure 4.4. The results also indicate the importance of diolefin structure as the less sterically hindered isoprene, with one double bond attached to a methyl group, was far more reactive in terms of oligomerization compared to the more sterically hindered 2,5-dimethyl-2,4-hexadiene, where both double bonds are attached to methyl groups.

Table 4.4 BET surface area, pore volume and pore size for the spent sulphided Ni-Mo-S/γ-Al2O3 catalyst before and after reactions.

<table>
<thead>
<tr>
<th>Ni-Mo-S/γ-Al2O3 (Spent) from Syncrude</th>
<th>BET Surface Area, m²/g</th>
<th>Pore volume, cm³/g</th>
<th>Pore size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before tests (TOS=0)</td>
<td>156 ± 6</td>
<td>0.28 ± 0.01</td>
<td>7.22 ± 0.02</td>
</tr>
<tr>
<td>After tests (TOS=1100 h⁻¹)</td>
<td>96 ± 4</td>
<td>0.16 ± 0.01</td>
<td>6.60 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4.5 Carbon, hydrogen, nitrogen and sulphur content for the spent sulphided Ni-Mo-S/γ-Al2O3 catalyst before and after reactions.

<table>
<thead>
<tr>
<th>Ni-Mo-S/γ-Al2O3 (Spent) from Syncrude</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>S (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before tests (TOS=0)</td>
<td>11.70 ± 0.18</td>
<td>0.82 ± 0.01</td>
<td>0.36 ± 0.02</td>
<td>5.14 ± 0.19</td>
</tr>
<tr>
<td>After tests (TOS=1100 h⁻¹)</td>
<td>14.98 ± 0.11</td>
<td>0.99 ± 0.03</td>
<td>0.42 ± 0.30</td>
<td>4.71 ± 0.11</td>
</tr>
</tbody>
</table>
Several experiments were also completed using 2.4 wt% isoprene in HTGO (diene value of 9 g I$_2$ / 100 g; equivalent to industrial naphtha feed). As before, it was impossible to identify and quantify the products using GC-MS as they overlapped the HTGO component peaks. Bromine number and diene value tests were performed on the samples and the results are summarized in Table 4.6. The decrease in bromine number and diene value in the product indicated hydrogenation activity. However, it's very difficult to determine the temperature effect on hydrogenation activity as the results are similar at both temperatures tested. In addition, oligomerization activity cannot be quantified due to issues with the measurement of gum content of the HTGO samples. The gum test was performed at a well temperature of 232°C according to ASTM D381-12, whereas the boiling range for the HTGO is 177-343°C, as indicated previously in Table 3.2. Hence, when the gum content tests were performed, the evaporation residue consisted of large quantities of liquid instead of gum. Therefore, in the experiments discussed in the next chapters, only decalin was used as a solvent so that both GC-MS analysis and gum content tests could be performed to examine the hydrogenation and oligomerization activities and relate them to catalyst deactivation and reactor fouling.
Table 4.6 Bromine number and diene value results (2.4 wt% isoprene in HTGO, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Temperature, °C</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>TOS, h</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>Cumulative TOS, h</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>Bromine number (g / 100 g)</td>
<td>4.5 ± 0.1</td>
<td>1.44 ± 0.05</td>
</tr>
<tr>
<td>Diene value (g I₂ / 100 g)</td>
<td>2.9 ± 0.1</td>
<td>0.75 ± 0.1</td>
</tr>
</tbody>
</table>

4.3 Summary

This chapter explored industrially relevant operating conditions that resulted in oligomer formation. Using fresh sulphided Ni-Mo-S catalyst supported on γ-Al₂O₃ (Criterion 424 hydrotreating catalyst), no oligomerization activity was detected during the hydrogenation of 17.8 wt% 2,5-dimethyl-2,4-hexadiene in decalin or HTGO at process conditions relevant to industrial hydrotreaters (T=150-250°C, P=3.4 MPa H₂ pressure, LHSV=2 hr⁻¹, and 600 standard mL/mL H₂/feed ratio).

When spent Ni-Mo-S/γ-Al₂O₃ catalyst, recovered from a Syncrude naphtha hydrotreater after shutdown, was tested, small amounts of oligomers (≤ 1.2wt% yield) were detected during the hydrogenation of 17.8 wt% 2,5-dimethyl-2,4-hexadiene or 5 wt% 2,5-dimethyl-2,4-hexadiene + 20 wt % 1-octene in decalin. This indicated that catalyst activity is linked to oligomerization
activity and that oligomers are formed when the hydrogenation activity declines due to catalyst deactivation. But due to the small amounts of oligomers, it was not possible to identify the oligomer structures using GC-MS or to establish a correlation between the oligomer content and the reaction conditions (T=180-250°C, P=3.4 MPa H2 pressure, LHSV=1-2 hr⁻¹, and 300-600 standard mL/mL H2/feed ratio).

In addition, the structure of the diolefin seemed to play a key role in oligomerization activity as a high degree of dimerization and a large decrease in catalyst activity were detected when isoprene, the less sterically hindered diolefin, was used in place of the more sterically hindered 2,5-dimethyl-2,4-hexadiene.

Since isoprene showed a tendency to dimerize, it was chosen as the model diolefin when investigating the effect of process conditions, namely temperature and diolefin content, on dimerization activity and reactor fouling (Chapter 5). Also, since it was impossible to identify and quantify oligomer and gum yields using GC-MS and the gum content tester when HTGO was used as a solvent, only decalin was used as a solvent in the following experiments. This allows the examination of hydrogenation and oligomerization activities by measuring the product yields and gum contents and relating them to catalyst deactivation and reactor fouling.
Chapter 5: Determining the effect process conditions on oligomer formation and reactor fouling during isoprene hydrogenation

In this chapter, the role of temperature and diolefin content on isoprene oligomerization and reactor fouling is examined. This is very important information needed to overcome the issue of catalyst deactivation and reactor fouling that leads to premature hydrotreater shutdown in industry. Isoprene was chosen as the model diolefin because it showed a tendency to oligomerize at industrial process conditions (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃) as discussed earlier in Chapter 4. Isoprene as reactant allows both hydrogenation and oligomerization catalyst activities to be determined.

5.1 Effect of temperature

Isoprene catalytic hydrogenation was carried out at industrial process conditions (P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The isoprene content of the feed oil was chosen as 2.4 wt% in decalin to reflect the diene value of a typical industrial naphtha feed (theoretical diene value = 9 g I₂ / 100 g). The reaction temperature was varied from 150 to 250°C and the catalyst activity was measured at different conditions without changing the catalyst bed. Some experiments were repeated toward the end of the run to check if there was any catalyst deactivation with TOS that might affect the catalyst activity in the sequential experiments.

The temperature effect on the hydrogenation and oligomerization activities is summarized in Figure 5.1. The hydrogenated product yield decreased from 93.3 ± 4.0 wt% to 80.1 ± 1.9 wt%
and the total oligomer yield increased from $3.6 \pm 0.7$ wt% to $17.3 \pm 0.8$ wt% as the temperature increased from 150 to 250°C. Most of the oligomers formed were isoprene dimers and $< 4$ wt% of higher oligomers was formed.

The increase in dimerization activity with temperature can be explained by the higher activation energy for dimerization reactions compared to hydrogenation. As discussed in Section 2.5, the activation energy for $\alpha$-methylstyrene hydrogenation is reported to be 15-61 kJ/mol whereas the oligomerization activation energy ranged from 76-99 kJ/mol. At higher temperature, more energy is available to overcome the activation barrier for dimerization and therefore dimerization activity increases. Similar observations have been made in the kinetic analysis of the present study reported in Chapter 8.

The corresponding average pressure drop results are shown in Figure 5.2. The average pressure drop was calculated as the average of the measured pressure drop per minute over 72 h TOS for each temperature. The average pressure drop across the reactor increased with increasing temperature, similar to the dimer formation reported in Figure 5.1. The result is consistent with increased deposition of carbonaceous material, formed as a result of oligomerization, within the catalyst bed causing reactor fouling and manifested by an increase in average pressure drop across the reactor.
Figure 5.1 Hydrogenated products and oligomer yield versus temperature (2.4 wt% isoprene in decalin, P=3.4 MPa, LHSV=2 hr\(^{-1}\), \(\text{H}_2/\text{feed}=392\) standard mL/mL, catalyst: spent Ni-Mo-S/\(\gamma\)-Al\(_2\)O\(_3\)).
To understand how isoprene may oligomerize, a look at the different oligomers produced from the reaction is necessary. Tables 5.1 and 5.2 summarize the oligomers obtained, their structure and yields versus temperature for dimers and \( \geq C_{10} \) oligomers, respectively. The main dimer produced was 1-methyl-3-isopropylcyclohexane. For this dimer, the yield increased with temperature from 1.0 ± 0.2 wt% at 150°C to 10.2 ± 0.4 wt% at 250°C. The same trend was
noticed for 1-ethyl-1,3-dimethylcyclohexane with the yield increasing form 0.6 ± 0.4 to 3.5 ± 0.5 wt% when the temperature increased from 200 to 250°C. Other dimers, trimers and tetramers, such as 2,6-, 3,6-, 2,7-dimethyloctane, 2,3,6-trimethylheptane, 2,6,10-trimethyldodecane, and 2,6,10,14-tetramethylhexadecane, were also produced in small quantities (< 2 wt%).

Before explaining how the products formed, it is important to highlight that the catalyst used, Ni-Mo-S/γ-Al₂O₃ is a bifunctional catalyst with two different sites: metallic sites provided by coordinatively unsaturated (cus) Ni-Mo, and acidic sites provided by the γ-Al₂O₃ support. As discussed earlier in Section 2.3, acidity can also be provided by the H₂S dissociative adsorption on Ni-Mo-S/γ-Al₂O₃ which can convert a sulphur vacancy to a -SH group and a Bronsted acid site. In addition, the promoter P₂O₅ can also be a source of Bronsted acid sites. Hydrogenation reactions are facilitated by the Ni-Mo-S sites [21] whereas oligomerization reactions are facilitated by acidic sites [35].

The proposed formation steps for 2,6-, 2,7-, 3,6-dimethyloctanes and 2,3,6-trimethylheptane are shown in Figure 5.3. These dimerizations can occur by the reaction of isoprene with a Bronsted acid to form an allylic carbocation. The conjugation aids in stabilizing the formed allylic carbocation by resonance. Resonance stabilizes the carbocation by delocalizing the π-electrons over several carbon atoms, thereby decreasing the electron deficiency [74]. The reaction then proceeds with the addition of another isoprene molecule to form a dimer with a secondary or a tertiary carbocation. The dimer carbocation reacts with a Bronsted base to form 2,6-, 2,7-, 3,6-dimethyloctatrienes or 2,3,6-trimethylheptatriene. The trienes are eventually hydrogenated over
metallic sites provided by the coordinatively unsaturated (cus) Ni-Mo to form the 2,6-, 2,7-, 3,6-dimethyloctanes and 2,3,6-trimethylheptance.

1-methyl-3-isopropylcyclohexane and 1-ethyl-1,3-dimethylcyclohexane can be formed by the cyclization and hydrogenation of 2,7-dimethyloctatriene and 2,6-dimethyloctatriene, respectively, similar to what was proposed by Bartholomew [35] as discussed earlier in Section 2.4.

Trimer 2,6,10-trimethyldodecane and tetramer 2,6,10,14-tetramethylhexadecane can be formed in the same manner as 2,6-dimethyloctanes but starting with the reaction of 2,6-dimethyloctatriene and 2,6,10-trimethyldodecatriene with a Bronsted acid to form an allylic carbocation, respectively.

Toward the end of the run, the experiments at 200 and 250°C were repeated to check if there was any catalyst deactivation with TOS that might have affected the catalyst activity in the sequential experiments. No significant change in the catalyst activity was detected as the standard errors calculated for isoprene conversion, hydrogenated products yield and oligomer yield were all < 2% for the repeated experiments at 200 and 250°C.
Table 5.1 Dimer structures and yields versus temperature (Feed: 2.4 wt% isoprene in decalin, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The dotted line shows the linkage location between the two isoprene molecules.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Name</th>
<th>Structure</th>
<th>150</th>
<th>180</th>
<th>200</th>
<th>230</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-methyl-3-isopropylcyclohexane</td>
<td><img src="image1" alt="Structure" /></td>
<td>1.0 ± 0.2</td>
<td>4.6 ± 0.8</td>
<td>6.5 ± 0.8</td>
<td>8.6 ± 0.6</td>
<td>10.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1-ethyl-1,3-dimethylcyclohexane</td>
<td><img src="image2" alt="Structure" /></td>
<td>0.2 ± 0.2</td>
<td>0</td>
<td>0.6 ± 0.4</td>
<td>2.6 ± 0.6</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>2,6-dimethyloctane + 3,6-dimethyloctane + 2,7-dimethyloctane</td>
<td><img src="image3" alt="Structure" /></td>
<td>1.3 ± 0.2</td>
<td>1.8 ± 0.3</td>
<td>1.4 ± 0.2</td>
<td>0.9 ± 0.2</td>
<td>0.7 ± 0</td>
</tr>
<tr>
<td></td>
<td>2,3,6-trimethylheptane</td>
<td><img src="image4" alt="Structure" /></td>
<td>0.6 ± 0.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 5.2 Other oligomer structures and yields versus temperature (Feed: 2.4 wt% isoprene in decalin, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The dotted line shows the linkage location between the two isoprene molecules.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>150</th>
<th>180</th>
<th>200</th>
<th>230</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6,10-trimethyldodecane</td>
<td>![Structure Image]</td>
<td>0.1 ± 0.1</td>
<td>0.4 ± 0.2</td>
<td>0</td>
<td>0.6 ± 0.6</td>
</tr>
<tr>
<td>2,6,10,14-tetramethylhexadecane</td>
<td>![Structure Image]</td>
<td>0.2 ± 0.1</td>
<td>1.7 ± 0.2</td>
<td>0.7 ± 0.2</td>
<td>0.8 ± 0.7</td>
</tr>
</tbody>
</table>

The dotted line shows the linkage location between the two isoprene molecules.
Figure 5.3 Proposed isoprene dimerization steps to form 2,6-, 2,7-, 3,6-dimethyloctane and 2,3,6-trimethylheptane.
5.2 Effect of diolefin content

Isoprene was hydrogenated at industrial process conditions (T=250°C, P=3.4 MPa, 
LHSV= 2 hr\(^{-1}\), H\(_2\)/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al\(_2\)O\(_3\)), but with the 
content of isoprene varied at 2.4, 3.6 and 4.8 wt% in decalin to reflect theoretical diene values of 
9 (the diene value of the industrial naphtha feed), 13.5 and 18 g I\(_2\) / 100 g. The temperature was 
fixed at 250°C because this temperature resulted in the highest oligomer yield among the 
temperatures tested previously in Section 5.1. This would facilitate the detection of oligomers 
with changing diolefin content.

As shown in Figure 5.4, the hydrogenation activity decreased as reflected in the decrease in 
hydrogenation product yield from 81.7 ± 0.4 to 59.3 ± 0.7 wt% 2-methylbutane as the theoretical 
diene value of the feed increased from 9 to 18 g I\(_2\) / 100 g. On the other hand, the oligomer 
content increased from 16.8 ± 0.5 to 38.8 ± 0.3 wt%. The gum content of the collected samples is 
reported in Figure 5.5. Although the obtained values were very small, the gum content seemed to 
increase with increasing diene value, following the trend seen previously in oligomer yield.

As the concentration of isoprene increased, the increase in dimerization reaction rate was higher 
than that of the hydrogenation reaction as seen by the larger increase in dimer yield versus 
hydrogenated products yield. This suggests that dimerization is of higher reaction order than 
hydrogenation.
Figure 5.4 Product yields versus theoretical diene value (2.4 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

Figure 5.5 Gum content versus theoretical diene value (2.4 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Table 5.3 lists the main dimers formed and their yields versus diene value. The highest yield obtained was for 1-methyl-3-isopropylcyclohexane. The yield almost doubled from 11.4 ± 0.4 to 23.4 ± 0.2 wt% when the amount of isoprene in the feed doubled. The second highest dimer obtained was 1-ethyl-1,3-dimethylcyclohexane, where the yield tripled from 4.1 ± 0.3 wt% to 12.4 ± 0.4 wt% when the isoprene amount in the feed doubled. Small amounts of 2,6- and 3,6-dimethyloctane were also formed. These dimers can be produced by carbocation formation and/or cyclization of trienes as discussed in Section 5.1.
Table 5.3 Dimer structures and yields versus theoretical diene value (Feed: 2.4, 3.6 and 4.8 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Diene value, g I₂ / 100 g</th>
<th>9</th>
<th>13.5</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methyl-3-isopropylcyclohexane</td>
<td><img src="image1.png" alt="Image" /></td>
<td>11.4 ± 0.4</td>
<td>13.5 ± 0.7</td>
<td>23.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>1-ethyl-1,3-dimethylcyclohexane</td>
<td><img src="image2.png" alt="Image" /></td>
<td>4.1 ± 0.3</td>
<td>7.8 ± 0.3</td>
<td>12.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>2,6-dimethyloctane  + 3,6-dimethyloctane</td>
<td><img src="image3.png" alt="Image" /></td>
<td>1.1 ± 0.3</td>
<td>0.7 ± 0.1</td>
<td>1.8 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>
5.3 Summary

To investigate the role of temperature, a feed consisting of 2.4 wt% isoprene in decalin was hydrogenated at industrially relevant process conditions (P=3.4 MPa, LHSV=2 hr\(^{-1}\), H\(_2\)/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/\(\gamma\)-Al\(_2\)O\(_3\)) while changing the temperature from 150°C to 250°C on the same catalyst bed. The content of isoprene was chosen to correspond to the diene value of a typical industrial naphtha feed (theoretical diene value = 9 g I\(_2\) / 100 g). As the temperature increased from 150 to 250°C, the hydrogenated products yield decreased from 93.3 ± 4.0 to 80.1 ± 1.9 wt% while the total oligomer yield increased from 3.6 ± 0.7 to 17.3 ± 0.8 wt%. The oligomers formed were mostly isoprene dimers. The increase in dimerization activity with temperature was explained by the higher activation energy for dimerization reactions compared to hydrogenation. At higher temperatures, more energy is available to overcome the activation barrier for dimerization and therefore dimerization activity increases.

The average pressure drop across the reactor increased with increasing temperature. This was explained by the increased deposition of carbonaceous material, formed as a result of oligomerization, within the catalyst bed causing reactor fouling.

The main dimers produced from isoprene were 1-methyl-3-isopropylcyclohexane and 1-ethyl-1,3-dimethylcyclohexane. For both dimers, the yield increased with temperature from 1.0 ± 0.2 wt% at 150°C up to 10.2 ± 0.4 wt% at 250°C and from 0.6 ± 0.4 up to 3.5 ± 0.5 wt% when the temperature increased from 200 to 250°C, respectively. 2,6-, 3,6-, 2,7-dimethyloctane and 2,3,6-trimethylheptane were also produced in small quantities (total < 2wt%). The dimerization was explained by the reaction of isoprene with a Bronsted acid to form an allylic carbocation,
reaction with another isoprene molecule to form a secondary or a tertiary carbocation which in turn reacts with a Bronsted base to form a triene. The triene is either hydrogenated or cyclized to form the final dimers.

To investigate the effect of diolefin content on oligomerization activity and reactor fouling, isoprene was then hydrogenated at industrial process conditions (T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). As the isoprene content increased from 2.4 to 4.2 wt%, the hydrogenation product yield decreased from 81.7 ± 0.4 to 59.3 ± 0.7 wt% 2-methylbutane. On the other hand, the oligomerization activity increased as reflected by the increase in oligomer yield from 16.8 ± 0.5 to 38.8 ± 0.3 wt%. The gum content followed the same trend as the oligomer yield and increased with increasing isoprene content. The higher increase in oligomerization reaction rate compared to that of hydrogenation, depicted by the product yields, as the concentration of isoprene increased, suggests that dimerization is of higher reaction order than hydrogenation.

The same dimers were detected as in the previous investigation, namely 1-methyl-3-isopropylcyclohexane and 1-ethyl-1,3-dimethylcyclohexane. The yield almost doubled from 11.4 to 23.4 wt% for 1-methyl-3-isopropylcyclohexane and tripled from 4.1 ± 0.3 to 12.4 ± 0.4 wt% for 1-ethyl-1,3-dimethylcyclohexane when the isoprene amount in the feed doubled. Small amounts of 2,6- and 3,6-dimethyloctane were also formed and their total yields followed the same trend as the other two main dimers.
Chapter 6: Effect of olefin/diolefin structure and content on oligomerization reactions

In this chapter, the effect of the olefin/diolefin structure, comparing linear versus cyclic conjugation, and sterically hindered olefins/diolefins, on the oligomerization reactions is examined. Different model olefins/diolefins were added to decalin and hydrogenated at industrially relevant process conditions (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The olefin/diolefin content was calculated to approximate the diene value in a typical industrial feed (diene value = 9 g I₂ / 100 g) [13]. In some tests, the olefin/diolefin content was increased to give a diene value of 18 g I₂ / 100 g, double the diene value in a typical naphtha feed, in order to increase the degree of oligomerization and investigate the different oligomers produced at higher olefin/diolefin concentration. All the tests discussed in this chapter were carried out sequentially on the same catalyst bed; i.e. the feed containing the olefin/diolefin was varied while maintaining the same reaction conditions and the same catalyst bed. Toward the end of the run, 20 wt% 1-octene was added to selected olefins/diolefins to investigate the role of mono-olefin addition on the oligomerization activity. The results aid in understanding how dimerization occurs for each model olefin/diolefin and how the structure affects the dimerization reactions that eventually lead to catalyst deactivation, reactor fouling and short hydrotreater catalyst lifespan.
6.1 Conjugated versus non-conjugated linear diolefins

To compare the effect of conjugation on dimerization reactions in linear diolefins, 1,3-pentadiene and 1,4-pentadiene were selected to represent the conjugated and non-conjugated linear diolefins, respectively. In each test, 2.4 wt% of the diolefin was added to decalin to achieve a diene value of 9 g I₂ / 100 g; the diene value of a typical industrial feed. The two tests were completed at the same industrially relevant process conditions (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The results of the tests are summarized in Table 6.1. The results show that 1,3-pentadiene was hydrogenated to pentane and 1-pentene with 93.1 ± 2.0 wt% total yield. Dimerization reactions also occurred, resulting mainly in 4,5-dimethyloctane and 4-methylnonane production. The total dimer yield reached 4.1 ± 1.0 wt%.

On the other hand, 1,4-pentadiene was mostly converted to pentane (99.7± 0.1 wt%) with a very small cyclopentane yield, most likely from cyclization reactions. No dimers were detected in the products from 1,4-pentadiene hydrogenation.

Since the reaction conditions were similar, the dimerization reaction activity can be attributed to the structure of the starting diolefin. To help understand how the structure affects the dimerization activity, a look at the reaction mechanism is necessary.
Table 6.1 Product yields and conversions for 1,3- and 1,4-pentadiene reactions (Feed: 2.4 wt% model diolefin in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>1,3-pentadiene</th>
<th>1,4-pentadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Structure</td>
<td>Yield, wt%</td>
<td></td>
</tr>
<tr>
<td>Pentane</td>
<td>92.0 ± 0.9*</td>
<td>99.7 ± 0.1</td>
</tr>
<tr>
<td>1-pentene + 3-pentene</td>
<td>1.1 ± 1.1</td>
<td>-</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>-</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>4,5-dimethyloctane</td>
<td>1.7 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>4-methylnonane</td>
<td>1.2 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>Other dimers</td>
<td>1.2 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>Total dimers</td>
<td>4.2 ± 0.9</td>
<td>0</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>99.4 ± 0</td>
<td>100 ± 0</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).

Figures 6.1 and 6.2 show the proposed reaction steps based on the detected dimers in the product. As shown in Figures 6.1 and 6.2, the proposed steps for dimerization reactions start with
the formation of an allylic carbocation by reaction with a Bronsted acid site. As discussed earlier in Section 2.3, acidity can be provided by the H₂S dissociative adsorption on Ni-Mo-S/γ-Al₂O₃ which can convert a sulphur vacancy to a -SH group and a Bronsted acid site. In addition, the promoter P₂O₅ and the γ-Al₂O₃ support can also be a source of Bronsted acid sites. The conjugation aids in stabilizing the formed allylic carbocation by resonance. Resonance stabilizes the carbocation by delocalizing the π-electrons over several carbon atoms, thereby decreasing the electron deficiency [74]. The formation of allylic carbocations from conjugated diolefins was also reported by Bartholomew [35] as discussed earlier in Section 2.4. The reaction then proceeds with the addition of another 1,3-pentadiene molecule to form a dimer with a secondary carbocation. The dimer carbocation reacts with a Bronsted base to form a triene. The triene is probably hydrogenated over metallic sites provided by the coordinatively unsaturated (cus) Ni-Mo to form the final dimer.

For linear diolefins, it was shown that conjugation plays a very important role in dimerization activity. The resonance created by conjugation possibly results in the formation of a stable allylic carbocation due to delocalization of the π-electrons which aid in decreasing the electron deficiency. This intermediate carbocation is key for the proposed diolefin dimerization steps.
6.2 Conjugated versus non-conjugated cyclic olefins/diolefins

To investigate the effect of conjugation on cyclic diolefins, 1,3- and 1,4-cyclohexadiene was hydrogenated. In these tests, 2.8 wt% of the chosen diolefin was added to decalin to obtain a diene value of 9 g I₂ / 100 g as before. Both tests were performed at the same industrial process conditions as before (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The results of the tests are summarized in Table 6.2. As shown in Table 6.2, 1,3-cyclohexadiene was mainly hydrogenated to cyclohexane with 95.6 ± 0.1 wt% total yield. Dimers and trimers were also detected. Dimers detected were 1-cyclohexylcyclohexene, 1,1'-bicyclohexyl and cyclohexylbenzene which constituted 2.8 ± 0.3 wt% total dimer yield. The only trimer identified was p-tercyclohexane with 0.2 ± 0 wt% yield.
Table 6.2 Product yields and conversions for 1,3- and 1,4-cyclohexadiene reactions (Feed: 2.8 wt% model diolefin in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>1,3-cyclohexadiene</th>
<th>1,4-cyclohexadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Structure</td>
<td>Yield, wt%</td>
</tr>
<tr>
<td>cyclohexene</td>
<td><img src="image" alt="cyclohexene" /></td>
<td>0.1 ± 0*</td>
</tr>
<tr>
<td>cyclohexane</td>
<td><img src="image" alt="cyclohexane" /></td>
<td>95.6 ± 0.3</td>
</tr>
<tr>
<td>1-cyclohexylcyclohexene</td>
<td><img src="image" alt="1-cyclohexylcyclohexene" /></td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>1,1'-bicyclohexyl</td>
<td><img src="image" alt="1,1'-bicyclohexyl" /></td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>cyclohexylbenzene</td>
<td><img src="image" alt="cyclohexylbenzene" /></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>p-tercyclohexane</td>
<td><img src="image" alt="p-tercyclohexane" /></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>&gt; C18</td>
<td>-</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>Total oligomers</td>
<td></td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>99.7 ± 0.2</td>
<td>99.7 ± 0.2</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
For 1,4-cyclohexadiene, the main product was cyclohexane with 99.2 ± 0.2 wt% yield. Only a small quantity of 1,1'-bicyclohexyl dimer was detected (0.2 ± 0 wt%).

The proposed reaction steps for the formation of dimers are shown in Figure 6.3. Similar to linear conjugated diolefins, the proposed dimerization reaction steps start with the formation of an allylic carbocation, stabilized by resonance, when reacted with a Bronsted acid. The reaction then proceeds with the addition of 1,3-cyclohexadiene to form a dimer with a secondary carbocation which converts to a triene when reacted with a Bronsted base. The triene is eventually hydrogenated over metallic sites provided by coordinatively unsaturated (cus) Ni-Mo to produce 1-cyclohexylcyclohexene or 1,1'-bicyclohexyl. The dimer can also be stabilized by dehydrogenation to convert the diolefin ring to a phenyl ring and form cyclohexylbenzene. The trimer is formed in a similar manner with the addition of two cyclohexadiene molecules as shown in Figure 6.4.

**Figure 6.3 Proposed dimer formation reaction steps (Feed: 2.8 or 5.7 wt% 1,3-cyclohexadiene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).**
Figure 6.4 Proposed trimer formation reaction steps (Feed: 2.8 or 5.7 wt% 1,3-cyclohexadiene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

Additional tests were performed at the same operating conditions with 3.8 wt% 1,3- and 1,5-cyclooctadiene in decalin. Table 6.3 shows the product yields and conversions for both diolefins. A high degree of hydrogenation with more than 98 wt% hydrogenated product yield was obtained for both diolefins. The dimer formation was very low and only detected from the 1,3-cyclooctadiene with only 0.1 wt% 1,1'-bicyclooctyl yield. This can be explained by looking at the computed 3d structure in Figure 6.5 which shows that the double bonds are not on the same plane. Therefore, the p-orbitals cannot overlap to delocalize the electrons and a stable allylic carbocation, the required dimerization intermediate, cannot be formed. The detected dimerization is most probably due to the formation of a secondary carbocation that reacts with another diolefin to form the dimer. The proposed reaction steps are shown in Figure 6.6.
Table 6.3 Product yields and conversions for 1,3- and 1,5-cyclooctadiene hydrogenation (Feed: 3.8 wt% model diolefin in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>Product</th>
<th>Structure</th>
<th>1,3-cyclooctadiene</th>
<th>1,5- cyclooctadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield, wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclooctane</td>
<td>97.0 ± 0.1*</td>
<td>94.0± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>octahydropentalene</td>
<td>2.0 ± 0</td>
<td>4.8 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1’-bicyclooctyl</td>
<td>0.1 ± 0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total oligomers</td>
<td>0.1 ± 0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion, %</td>
<td>100 ± 0</td>
<td>99.9 ± 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
Figure 6.5 Computed 3d structure for cis, cis-1,3-cyclooctadiene.

Figure 6.6 Proposed 1,1'-bicyclooctyl formation reaction steps (Feed: 3.8 wt% 1,3-cyclooctadiene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Finally, experiments using styrene and 4-vinylcyclohexene were completed to confirm the role of conjugation. As seen in Table 6.4, the structure of 4-vinylcyclohexene shows that this molecule is non-conjugated since the double bonds are separated by 3 single bonds and therefore the interaction between p-orbitals is not possible. Styrene on the other hand has a phenyl ring with an ethylene group. Resonance exists between all the double bonds due the interaction of all p-orbitals. The experiments were performed at the same industrial conditions as before (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The content of model reactants used was 7.7 wt% and 7.4 wt% for the 4-vinylcyclohexene and styrene, respectively. These concentrations reflect a diene value of 18 g I₂ / 100 g, double the amount of diene value in the real industrial feed. The diene value was doubled in these tests to investigate the effect of olefin/diolefin concentration on oligomerization product yields. The results of the experiments are summarized in Table 6.4. As expected, 94.1 ± 0.4 wt% 4-vinylcyclohexene was hydrogenated to ethylcyclohexane. A smaller yield, 5.2 ± 0.4 wt%, of ethylbenzene was also detected which shows that stabilization by dehydrogenation and phenyl ring formation is also possible. As seen before for non-conjugated diolefins, no oligomers were detected for 4-vinylcyclohexene. On the other hand, due to the presence of the stable phenyl ring, styrene was mainly converted to ethylbenzene with 60.0 ± 4.9 wt% yield and partly to ethylcyclohexane with 30.5 ± 6.4 wt% yield. Due to the stability of the intermediate allylic carbocation, styrene also oligomerized to form 10.4 ± 2.9 wt% oligomers, mainly (3-phenylbutyl)benzene. The formation steps of (3-phenylbutyl)benzene are shown in Figure 6.7. As with other conjugated olefins/diolefins, the reaction starts with the formation of an allylic carbocation by reacting with a Bronsted acid provided by the acidic catalyst sites. Another
styrene molecule is then added and the intermediate dimer reacts with Bronsted base and hydrogenates to form (3-phenylbutyl)benzene.

For cyclic olefins/diolefins, it was shown that conjugation plays a similar role in dimerization activity as in linear diolefins. The resonance aids in stabilizing the formed allylic carbocation by spreading the positive charge and decreasing the electron deficiency. The formation of an allylic carbocation can explain the dimer formation.

![Proposed reaction steps](image)

**Figure 6.7 Proposed (3-phenylbutyl)benzene formation reaction steps (Feed: 7.4 wt% styrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).**
Table 6.4 Product yields and conversions for 4-vinylcyclohexene and styrene hydrogenation (T=250°C, P=3.4 MPa, LHSV=2 hr\(^{-1}\), \(\text{H}_2/\text{feed}=392\) standard mL/mL, catalyst: spent Ni-Mo-S/\(\gamma\)-Al\(_2\)O\(_3\)).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>4-vinylcyclohexene</th>
<th>styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Structure</td>
<td>Yield, wt%</td>
</tr>
<tr>
<td>Ethylcyclohexane</td>
<td><img src="image" alt="Ethylcyclohexane" /></td>
<td>94.1 ± 0.4*</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td><img src="image" alt="Ethylbenzene" /></td>
<td>5.2 ± 0.4</td>
</tr>
<tr>
<td>(3-phenylbutyl)benzene</td>
<td><img src="image" alt="3-phenylbutylbenzene" /></td>
<td>-</td>
</tr>
<tr>
<td>Other dimers</td>
<td>-</td>
<td>3.0 ± 0.9</td>
</tr>
<tr>
<td>&gt; C16</td>
<td>-</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>Total oligomers</td>
<td>-</td>
<td>10.4 ± 2.9</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>100 ± 0</td>
<td>100 ± 0</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
6.3 Effect of 1,3-cyclohexadiene content on oligomerization

To study the effect of diolefin concentration on the oligomerization yield, 1,3-cyclohexadiene hydrogenation was repeated with double the diene value by increasing the diolefin content to 5.7 wt%. The other conditions were kept the same as before (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The results for the tests with diene values of 9 and 18 g I₂ / 100 g are both shown in Table 6.5 for easier comparison. By doubling the amount of diolefin in the feed from 2.8 wt% to 5.7 wt%, the total oligomer yield almost doubled from 3.5 ± 0.4 wt% to 6.7 ± 0.3 wt%. This is in agreement with the results obtained for isoprene in Section 5.2. Looking more closely at the results in Table 6.5, it can be seen that the hydrogenated products yield decreased by 3.7 ± 0.5 wt%. The dimer product yield increased with the highest increase detected for 1-cyclohexylcyclohexene which increased more than three fold. Trimer formation also increased from 0.2 wt% to more than 1 wt% and the formation of a new trimer, octadecahydrotriphenylene was observed with an increase in diolefin in the feed. The proposed formation steps for octadecahydrotriphenylene are shown in Figure 6.4. The reaction starts with the formation of an allylic carbocation, stabilized by resonance, when reacted with Bronsted acid. The reaction then proceeds with the addition of two 1,3-cyclohexadiene molecules to form a trimer with a secondary carbocation which converts to a triene when reacted with a Bronsted base. The triene is eventually hydrogenated over metallic sites provided by 3-co-ordinatively unsaturated (3-cus) Ni-Mo to give octadecahydrotriphenylene.
Similar to the results obtained for isoprene in Section 5.2, the increase in oligomerization reaction rate was higher than that of hydrogenation, as depicted by the oligomerization and hydrogenated products yield, respectively, when the 1,3-cyclohexadiene content in the feed was increased. This suggests that oligomerization is of higher reaction order than hydrogenation.
Table 6.5 Product yields and conversions for 1,3-cyclohexadiene hydrogenation (Feed: 2.8 and 5.7 wt% 1,3-cyclohexadiene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed content, wt%</th>
<th>2.8</th>
<th>5.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Structure</td>
<td>Yield, wt%</td>
</tr>
<tr>
<td>cyclohexene</td>
<td></td>
<td>0.1 ± 0*</td>
</tr>
<tr>
<td>cyclohexane</td>
<td></td>
<td>95.6 ± 0.3</td>
</tr>
<tr>
<td>1-cyclohexylcyclohexene</td>
<td></td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>1,1'-bicyclohexyl</td>
<td></td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>cyclohexylbenzene</td>
<td></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>p-tercyclohexane</td>
<td></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>octadecahydrotriphenylene</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>&gt; C18</td>
<td></td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>Total oligomers</td>
<td></td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>Conversion, %</td>
<td></td>
<td>99.7 ± 0.2</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
6.4 Steric hindrance on cyclic diolefin oligomerization

To investigate the possible role of steric hindrance in oligomerization, a hydrogenation test was completed using α-terpinene as feed diolefin compared with 1,3-cyclohexadiene. The structure of α-terpinene is similar to that of 1,3-cyclohexadiene, except that in α-terpinene the double bonds are attached to a methyl group and an isopropyl group. Both tests were performed at the same industrial process conditions as before (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃), but with double the diene value of the industrial feed to increase the oligomerization content for easier quantification of the products. The results for 1,3-cyclohexadiene and α-terpinene are summarized in Tables 6.5 and 6.6, respectively.

As shown in Table 6.6, 71.1 ± 0.3 wt% of α-terpinene was converted to 1-methyl-4-isopropylcyclohexane and 28.3 ± 0.3 wt% was stabilized by dehydrogenation and converted to 1-methyl-4-isopropylbenzene. A very small quantity dimerized and formed 3,3′-bi-p-menthane (yield of 0.1 wt%). The dimerization yield was much less than the total oligomerization yield of 1,3-cyclohexadiene, shown in Table 6.5, which reached 6.7 ± 0.3 wt%. This difference in oligomerization activity can be attributed to the steric hindrance provided by the methyl and isopropyl groups attached to the double bonds of the cyclohexene. These groups limit access to and reactivity with the double bonds and therefore less oligomers are formed.
Table 6.6 Product yields and conversions for α-terpinene hydrogenation (Feed: 9.7 wt% α-terpinene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>Name</th>
<th>α-terpinene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Structure</td>
</tr>
<tr>
<td>Product</td>
<td>Structure</td>
<td>Yield, wt%</td>
</tr>
<tr>
<td>1-methyl-4-isopropylcyclohexane</td>
<td><img src="image" alt="Structure" /></td>
<td>71.1 ± 0.3*</td>
</tr>
<tr>
<td>1-methyl-4-isopropylbenzene</td>
<td><img src="image" alt="Structure" /></td>
<td>28.3 ± 0.3</td>
</tr>
<tr>
<td>1-methyl-4-isopropyl-cyclohexene</td>
<td><img src="image" alt="Structure" /></td>
<td>0.1 ± 0</td>
</tr>
<tr>
<td>3,3'-bi-p-menthane</td>
<td><img src="image" alt="Structure" /></td>
<td>0.1 ± 0</td>
</tr>
<tr>
<td>Total oligomers</td>
<td></td>
<td>0.1 ± 0</td>
</tr>
<tr>
<td>Conversion, %</td>
<td></td>
<td>100 ± 0</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
6.5 Oligomerization of 4-methylstyrene

The last structure examined was 4-methylstyrene. 4-methylstyrene represents an interesting structure that is similar to styrene, which showed the highest degree of oligomerization, but with an additional methyl group. 4-methylstyrene was hydrogenated at the standard conditions (T ≤ 250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃) with double the diene value to increase the degree of oligomerization and examine the different products even if present in small quantities.

The results of the test are reported in Table 6.7. 4-methylstyrene was mainly hydrogenated to 1-ethyl-4-methylbenzene (70.3 ± 2.9 wt% yield) and much less completely hydrogenated to 1-ethyl-4-methylcyclohexane (6.1 ± 0.3 wt% yield). Oligomerization was relatively high compared to other structures tested, with a total yield of 23.2 ± 3.7 wt%. The main dimer formed was 1,3-di-(4'-methylphenyl)butane with a yield of 12.8 ± 0.5 wt%. The proposed formation steps for the different dimers are shown in Figure 6.8. As in the case of styrene, the reaction starts with the formation of an allylic carbocation by reaction with a Bronsted acid site, but note that the positive charge can also be shared with the additional methyl group of the 4-methylstyrene structure due to hyperconjugation [74]. This gives higher carbocation stability by delocalizing the π-electrons over more carbon atoms and therefore decreasing the electron deficiency compared to styrene. The reaction then proceeds with the addition of a 4-methylstyrene molecule and reacting with Bronsted base to form 1,3- or 1,4-di-(4'-methylphenyl)butene, the former detected in small quantities as shown in Table 6.7. 1,3- and 1,4-di-(4'-methylphenyl)butene are then hydrogenated to form 1,3- and 1,4-di-(4'-methylphenyl)butane, respectively.
4-methylstyrene showed the highest degree of oligomerization among all other olefins/diolefins tested. This gives insight into the importance of resonance and π-electron delocalization in forming the intermediate allylic carbocation that leads to dimerization and other oligomerization reactions. Due to its high oligomerization activity, 4-methylstyrene was selected for catalyst deactivation and reaction fouling tests, and for the reaction kinetics investigations discussed later in Chapters 7 and 8.

Figure 6.8 Proposed dimer formation reaction steps (Feed: 8.4 wt% 4-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Table 6.7 Product yields and conversions for 4-methylstyrene hydrogenation (Feed: 8.4 wt% 4-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Model feed</th>
<th>Name</th>
<th>4-methylstyrene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Structure</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Product</td>
<td>Structure</td>
<td>Yield, wt%</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td><img src="image" alt="Structure" /></td>
<td>70.3 ± 2.9*</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td><img src="image" alt="Structure" /></td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td><img src="image" alt="Structure" /></td>
<td>12.8 ± 0.5</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butene</td>
<td><img src="image" alt="Structure" /></td>
<td>0.1 ± 0</td>
</tr>
<tr>
<td>1,4-di-(4'-methylphenyl)butane</td>
<td><img src="image" alt="Structure" /></td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>&gt;C18</td>
<td><img src="image" alt="Structure" /></td>
<td>9.2 ± 3.0</td>
</tr>
<tr>
<td>Total oligomers</td>
<td><img src="image" alt="Structure" /></td>
<td>23.2 ± 3.7</td>
</tr>
<tr>
<td>Conversion, %</td>
<td><img src="image" alt="Structure" /></td>
<td>99.9 ± 0</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
6.6 1-octene addition

Toward the end of the experimental run, a few tests were repeated with the addition of 20 wt% 1-octene to represent the olefin content in a real naphtha feed and to investigate the role of mono-olefin addition on the oligomerization activity. The product yield of the 1,3-cyclohexadiene and styrene, with and without 1-octene addition, are shown in Table 6.8 and Table 6.9, respectively. The results show that the oligomer yields were very similar, within experimental error, with and without the addition of 1-octene. A closer look at the oligomers obtained does not show that there was any interaction between 1-octene and 1,3-cyclohexadiene or styrene to form a new oligomer. In fact, 1-octene was totally hydrogenated to octane in all tests. Therefore, 1-octene addition to the feed does not seem to affect hydrogenation or dimerization activities of the conjugated olefins/diolefins.
Table 6.8 Product yields and conversions for 1,3-cyclohexadiene hydrogenation (Feed: 2.8 wt% 1,3-cyclohexadiene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>with 20 wt% 1-octene</td>
</tr>
<tr>
<td>cyclohexene</td>
<td><img src="image" alt="cyclohexene" /></td>
<td>0.1 ± 0*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>cyclohexane</td>
<td><img src="image" alt="cyclohexane" /></td>
<td>95.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.3 ± 0.4</td>
</tr>
<tr>
<td>1-cyclohexylcyclohexene</td>
<td><img src="image" alt="1-cyclohexylcyclohexene" /></td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>1,1'-bicyclohexyl</td>
<td><img src="image" alt="1,1'-bicyclohexyl" /></td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>cyclohexylbenzene</td>
<td><img src="image" alt="cyclohexylbenzene" /></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td>p-tercyclohexane</td>
<td><img src="image" alt="p-tercyclohexane" /></td>
<td>0.2 ± 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>&gt; C18</td>
<td>-</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Total oligomers</td>
<td></td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.5 ± 0.5</td>
</tr>
<tr>
<td>Conversion, %</td>
<td></td>
<td>99.7 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99.6 ± 0.2</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
Table 6.9 Product yields and conversions for styrene hydrogenation (Feed: 7.4 wt% styrene in deca
lin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt% with 20 wt% 1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylcyclohexane</td>
<td><img src="image" alt="Ethylcyclohexane" /></td>
<td>30.5 ± 6.4*</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td><img src="image" alt="Ethylbenzene" /></td>
<td>60.0 ± 4.9</td>
</tr>
<tr>
<td>(3-phenylbutyl)benzene</td>
<td><img src="image" alt="3-phenylbutyl benzene" /></td>
<td>6.0 ± 1.6</td>
</tr>
<tr>
<td>Other dimers</td>
<td></td>
<td>3.0 ± 0.9</td>
</tr>
<tr>
<td>&gt; C16</td>
<td></td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>Total oligomers</td>
<td></td>
<td>10.4 ± 2.9</td>
</tr>
<tr>
<td>Conversion, %</td>
<td></td>
<td>100 ± 0</td>
</tr>
</tbody>
</table>

*Standard error calculated based on the results of experiments from 3 consecutive days TOS on the same catalyst bed at the same process conditions (refer to Appendix C for more details).
6.7 Summary

In this chapter, the oligomerization activity was examined for conjugated and non-conjugated linear and cyclic olefins/diolefins. Conjugation was shown to play an important role in oligomerization. The resonance generated by conjugation aids in stabilizing the formed allylic carbocation due to π-electron delocalization and positive charge spreading to reduce the electron deficiency. The proposed allylic carbocation formation is a key step in dimerization and oligomerization reactions.

The effect of cyclic diolefin concentration was investigated and it was found that a larger increase in oligomer formation was detected compared to hydrogenated products yield when the concentration of the diolefin in the feed increased. This indicated that the order of oligomerization reaction rate is higher than that of hydrogenation.

Steric hindrance was also shown to play a role in limiting the degree of oligomerization. α-terpinene showed far less oligomer yield compared to 1,3-cyclohexadiene. This was explained by the steric hindrance created by the methyl and isopropyl groups attached to the double bonds of α-terpinene.

The experiments performed with 4-methylstyrene showed that this conjugated olefin gave the highest oligomer yield compared to all other olefins/diolefins tested. This was explained by the higher stabilization of the allylic carbocation formed compared to other olefins/diolefins tested due to the delocalization of the π-electron and the spread of the positive charge among more carbon atoms.
The addition of 1-octene to several conjugated olefins/diolefins did not show any significant change in oligomerization yield. 1-octene was hydrogenated to octane and the oligomer products suggested that the 1-octene was not involved in the dimerization reaction.
Chapter 7: Catalyst deactivation and reactor fouling with model reactants

In previous chapters, the effect of various feed compositions and process conditions were measured sequentially on the same load of catalyst in the reactor. This makes the quantification of catalyst deactivation and reactor fouling difficult due to the cumulative carbon deposition on the catalyst and within the catalyst bed during the experimental run.

This chapter explores the catalyst deactivation and reactor fouling that results from the dimerization of model conjugated olefins diluted in decalin during hydrotreating reactions. The tests were completed over periods of 3, 12, 21, and 30 days TOS at the same process conditions (T =200-250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). For each set of operating conditions, a new catalyst bed was loaded into the reactor and the spent catalyst was recovered for characterization after the desired TOS period. Since 4-methylstyrene showed the highest degree of dimerization, it was selected as the model reactant. One test was completed using α-methylstyrene as a model reactant to investigate the effect of steric hindrance, resulting from the methyl group attached to the vinyl group, on catalyst deactivation and reactor fouling. The tests were performed using model reactants diluted in decalin instead of real hydrotreater feed to facilitate product characterization and result interpretation.

Most of the tests were performed with 8.4 wt% model reactant content which represents a diene value of 18 g I₂ / 100 g, double the diene value in a typical naphtha feed [13], in order to enhance
the degree of dimerization. This aids in the investigation of the impact of conjugated olefin dimerization on catalyst deactivation and reactor fouling.

One test was completed using 4.2 wt% 4-methylstyrene, which approximates the actual diene value in an industrial feed (diene value = 9 g I$_2$ / 100 g) [13] and provides data to quantify the effect of conjugated olefin content on catalyst deactivation and reactor fouling.

In some tests, 20 wt% cyclohexene was added to the feed to represent the olefin content in the real naphtha feed [13] and to determine the impact of olefin content on catalyst deactivation and reactor fouling.

### 7.1 Role of steric hindrance

To investigate the effect of steric hindrance on dimerization, catalyst deactivation and reactor fouling, the tests in this section were completed using 8.4 wt% 4-methylstyrene or α-methylstyrene in decalin. The α-methylstyrene has some degree of steric hindrance resulting from the methyl group attached to the vinyl group limiting access and reactivity of the double bond. The content of the conjugated olefin represents double the diene value of a typical naphtha feed [13], in order to increase the degree of dimerization and study the impact on catalyst deactivation and reactor fouling in a relatively short period of reactor TOS.

Figure 7.1 shows that the dimer yield and gum content is significantly higher for 4-methylstyrene than α-methylstyrene. The 4-methylstyrene produced dimers with a yield of $11.2 \pm 0.4$ to $32.4 \pm 1.2$ wt% and a gum content of $2626 \pm 35$ to $3152 \pm 42$ mg/100 mL whereas α-methylstyrene
resulted in a < 2 wt% dimer yield and < 40 mg/100 mL gum over 30 days TOS. Since the reaction conditions were identical, the differences support the proposal that the methyl group attached to the vinyl group creates steric hindrance that prevents the dimerization of α-methylstyrene.

The detailed product yields, conversions, gum contents, bromine numbers and diene values as a function of TOS are listed in Table 7.1 for 4-methylstyrene and in Table 7.2 for α-methylstyrene. At the chosen operating conditions, the conversions for both 4-methylstyrene and α-methylstyrene reached 100% and remained at that level until the end of the test (30 days TOS). After 3 days TOS, 4-methylstyrene was mainly hydrogenated to 1-ethyl-4-methylbenzene with a yield of 78.0 ± 2.8 wt%. The completely hydrogenated product 1-ethyl-4-methylcyclohexane was also formed with a yield of 10.7 ± 0.4 wt%. The main dimerization product from 4-methylstyrene was 1,3-di-(4'-methylphenyl)butane produced with a yield of 10.0 ± 0.4 wt%. Another dimer, 1,4-di-(4'-methylphenyl)butane, was also detected with a yield of 1.2 wt%. After 30 days TOS, less hydrogenated products were formed with the yield of 1-ethyl-4-methylbenzene decreasing to 56.6 ± 2.0 wt% whereas the yield of dimers increased to 30.3 ± 1.1 wt% and 2.1 ± 0.1 wt% for 1,3-di-(4'-methylphenyl)butane and 1,4-di-(4'-methylphenyl)butane, respectively. The same products were detected for 4-methylstyrene in the sequential experiments reported earlier in Section 6.5 but with additional formation of other oligomers (> C18). This can be attributed to the different degree of catalyst deactivation in the two cases.
Figure 7.1 Dimer yield and gum content for 4- and α-methylstyrene reactions (Feed: 8.4 wt% model reactant in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
$^{13}$C-NMR analysis of the liquid product (day 30 TOS) confirmed the presence of 1-ethyl-4-methylbenzene as shown in Figure 7.2 and Table 7.3 (higher resolution figures are included in Appendix G). Other peaks of the $^{13}$C-NMR spectrum can be assigned to decalin as shown in Table 7.4 or to $^{13}$C-NMR solvent, CD$_2$Cl$_2$ (53.30-54.38 ppm). The dimers were not detected by $^{13}$C-NMR due to their small quantity in the liquid product. Therefore, a diluted gum sample was analyzed to determine the presence of dimers. The $^{13}$C-NMR spectrum is shown in Figure 7.3 (higher resolution figures are included in Appendix G). Most of the peaks in the spectrum can be assigned to 1,3-di-(4'-methylphenyl)butane as shown in Table 7.5. The peaks at 53.30-54.38 ppm belong to CD$_2$Cl$_2$ ($^{13}$C-NMR solvent). Other peaks most probably relate to the other dimer, 1,4-di-(4'-methylphenyl)butane, but due to the small quantity the peaks were small and difficult to assign. The assignment was completed with aid of the Spectral Database for Organic Compounds, SDBS [76]. Since the gum content determination involves evaporating the sample under controlled temperature (232° C well temperature) and steam flow (1000 mL/s), elemental CHNS analysis was also completed on the same gum sample to estimate the oxygen content of the gum that might be present because of reaction with steam or trace oxygen in the reactant feed. The contents were found to be 87.45 ± 0.79 wt%, 10.59 ± 0.77 wt%, 0.94 ± 0.02 wt% and 1.01 ± 0.01 wt% for carbon, hydrogen, nitrogen and sulphur, respectively. The results confirm that the gum consists mainly of carbon and hydrogen and that the oxygen content is insignificant.

The dimer yield increase was also accompanied by an increase in gum content from 2626 ± 35 mg/100 mL after 3 days TOS to 3152 ± 42 mg/100 mL after 30 days TOS. The high hydrogenation activity was reflected in the decrease in both bromine number and diene value to 0 from the feed values of 11.4 ± 0.4 g/100 g and 8.9 ± 1.1 g I$_2$ / 100 g, respectively. After 30
days TOS, both bromine number and diene value remained low but increased slightly to 0.7 g/100 g and 0.3 I$_2$ / 100 g to reflect a very small decrease in hydrogenation activity. Note that the bromine number is an empirical measurement of the aliphatic unsaturation and therefore the aromatic unsaturation found in the product doesn’t contribute to the bromine number.

For α-methylstyrene, the main hydrogenated products were (1-methylethyl)benzene with 81.6 ± 2.9 wt% yield and (1-methylethyl)cyclohexane with 17.1 ± 0.6 wt% yield, after 3 days TOS. The total hydrogenated product yield remained almost the same after 30 days TOS but with increasing selectivity toward (1-methylethyl)benzene (84.4 ± 3.0 wt% yield) versus (1-methylethyl)cyclohexane (13.8 ± 0.5 wt% yield). The dimer formation remained low throughout with 2,4-diphenyl-4-methyl-2-pentene and 2,4-diphenyl-4-methylpentane dimers formed with < 2 wt% yield. The gum content reflected the low yield of dimer formation with < 40 mg/100 mL gum formed. Both bromine number and diene value decreased from the feed values and remained < 0.2 g/100 g or I$_2$ /100 g, reflecting the stablility of the catalyst hydrogenation activity.

The formation steps for 4-methylstyrene dimers was previously discussed in Section 6.5. The proposed reaction steps for the dimerization of α-methylstyrene are shown in Figure 7.4. Similar to other conjugated olefins/diolefins, the proposed reaction steps assume the formation of an allylic carbocation by reaction with a Bronsted acid. The reaction proceeds with the addition of α-methylstyrene and by reacting with a Bronsted base to form 2,4-diphenyl-4-methyl-2-pentene. Part of 2,4-diphenyl-4-methyl-2-pentene is then hydrogenated to form 2,4-diphenyl-4-methylpentane. As seen in the proposed mechanism in Figure 7.4, the methyl group attached to

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the vinyl group not only limits activation of the double bond, but also the addition of α-methylstyrene to the allylic carbocation to form a dimer (step 2).
Table 7.1 Product yields and conversions for 4-methylstyrene reaction (Feed: 8.4 wt% 4-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
<th>TOS, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td>-</td>
<td>78.0 ± 2.8</td>
<td>64.3 ± 2.3</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td>-</td>
<td>10.7 ± 0.4</td>
<td>14.2 ± 0.5</td>
</tr>
<tr>
<td>1,3-di-(4′-methylphenyl)-butane</td>
<td>-</td>
<td>10.0 ± 0.4</td>
<td>19.7 ± 0.7</td>
</tr>
<tr>
<td>1,4-di-(4′-methylphenyl)-butane</td>
<td>-</td>
<td>1.2 ± 0</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>Total dimers, wt%</td>
<td>-</td>
<td>11.2 ± 0.4</td>
<td>21.5 ± 0.8</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>-</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Gum content mg/100 mL</td>
<td></td>
<td>204 ± 2</td>
<td>2626 ± 35</td>
</tr>
<tr>
<td>Bromine number, g / 100 g</td>
<td></td>
<td>11.4 ± 0.4</td>
<td>0</td>
</tr>
<tr>
<td>Diene value, g I₂ / 100 g</td>
<td></td>
<td>8.9 ± 1.1</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 7.2 Product yields and conversions for α-methylstyrene reactions (Feed: 8.4 wt% α-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>TOS, days</td>
<td>0</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>(1-methylethyl)-benzene</td>
<td>-</td>
<td>81.6 ± 2.9</td>
<td>83.0 ± 2.9</td>
<td>83.3 ± 2.9</td>
<td>84.4 ± 3.0</td>
</tr>
<tr>
<td>(1-methylethyl)-cyclohexane</td>
<td>-</td>
<td>17.1 ± 0.6</td>
<td>15.9 ± 0.6</td>
<td>15.3 ± 0.5</td>
<td>13.8 ± 0.5</td>
</tr>
<tr>
<td>2,4-diphenyl-4-methyl-2-pentene</td>
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<td>1.3 ± 0</td>
<td>1.1 ± 0</td>
<td>0.8 ± 0</td>
<td>1.0 ± 0</td>
</tr>
<tr>
<td>2,4-diphenyl-4-methylpentane</td>
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<td>0</td>
<td>0</td>
<td>0.6 ± 0</td>
<td>0.7 ± 0</td>
</tr>
<tr>
<td>Total dimers, wt%</td>
<td>-</td>
<td>1.3 ± 0</td>
<td>1.1 ± 0</td>
<td>1.4 ± 0.1</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Conversion, %</td>
<td>-</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Gum content mg/100 mL</td>
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<td>46 ± 1</td>
<td>34 ± 0</td>
<td>15 ± 0</td>
<td>28 ± 0</td>
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<tr>
<td>Bromine number, g / 100 g</td>
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<td>11.9 ± 0.4</td>
<td>0.2 ± 0</td>
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<tr>
<td>Diene value, g I₂ / 100 g</td>
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<td>2.5 ± 0.3</td>
<td>0.2 ± 0</td>
<td>0.2 ± 0</td>
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Figure 7.2 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS.
Table 7.3 $^{13}$C-NMR spectrum assignment 1-ethyl-4-methylbenzene.

<table>
<thead>
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<th>Name</th>
<th>Structure</th>
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</thead>
<tbody>
<tr>
<td>1-ethyl-4-methylbenzene</td>
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<th>ppm</th>
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<td>129.57</td>
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<td>128.31</td>
<td>4</td>
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</tr>
<tr>
<td>21.36</td>
<td>6</td>
</tr>
<tr>
<td>16.33</td>
<td>7</td>
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</table>

Table 7.4 $^{13}$C-NMR spectrum assignment for decalin.

<table>
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<tr>
<td>Decalin</td>
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<table>
<thead>
<tr>
<th>ppm</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>44.31</td>
<td>1-trans</td>
</tr>
<tr>
<td>37.15</td>
<td>1-cis</td>
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<tr>
<td>34.98</td>
<td>2</td>
</tr>
<tr>
<td>27.52</td>
<td>3</td>
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</table>
Figure 7.3 $^{13}$C-NMR spectrum for the gum recovered from 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS.
Table 7.5 $^{13}$C-NMR spectrum assignment 1,3-di-(4'-methylphenyl)butane.

<table>
<thead>
<tr>
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<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td><img src="chart.png" alt="Chart" /></td>
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</table>

<table>
<thead>
<tr>
<th>ppm</th>
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<tbody>
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<td>146.06</td>
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</tr>
<tr>
<td>135.36</td>
<td>3</td>
</tr>
<tr>
<td>129.22</td>
<td>4</td>
</tr>
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<td>128.04</td>
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<tr>
<td>24.07</td>
<td>10</td>
</tr>
<tr>
<td>21.23</td>
<td>11</td>
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</table>
Figure 7.4 Proposed dimer formation reaction steps (Feed: 8.4 wt% α-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

7.2 The effect of olefin addition

In order to represent the olefin content in the real naphtha feed and study its impact on catalyst deactivation and reactor fouling, experiments were conducted with the addition of 20 wt% cyclohexene to the 4-methylstyrene feed. Figure 7.5 shows the conversion, gum content, dimer yield and selectivity of the 4-methylstyrene reactions, with and without cyclohexene addition. The detailed product yields, conversion, gum content, bromine numbers and diene values are listed in Table 7.1 for 4-methylstyrene and in Table 7.6 for 4-methylstyrene with cyclohexene addition. Note that cyclohexene was only converted to cyclohexane therefore the yield of cyclohexane is equal to the cyclohexene conversion. As shown in Figure 7.5, the conversion of 4-methylstyrene significantly decreased with TOS in the case of cyclohexene addition, from 100% after 3 days TOS to 75.3 ± 2.7 w% after 30 days TOS. This indicates a severe loss in catalyst activity. The loss of catalyst activity caused a significant decrease in hydrogenation activity as shown by the decrease in hydrogenated product yield, namely 1-ethyl-4-methylbenzene, in Table 7.6. The loss in hydrogenation activity was also reflected in the increase in bromine number from 0.9 g/100 g after 3 days TOS to 33.5 ± 1.1 g/100 g after 30 days TOS. The diene value also increased from 0 to 2.5 ± 0.3 g I₂ / 100 g, respectively.
On the other hand, the dimer yield increased from 6.5 ± 0.2 wt% after 3 days TOS to 25.7 ± 0.9 wt% yield after 30 days TOS. However, the total dimer yield was slightly less in the case of cyclohexene addition compared to the experiments completed with no cyclohexene added, as shown in Figure 7.5. The figure also shows that less gum was recovered from the products with cyclohexene addition to the feed versus the experiments without cyclohexene addition. Comparing the gum content to 4-methylstyrene conversion, Figure 7.5 shows that as the conversion decreased, more gum was formed in the 4-methylstyrene + cyclohexene tests. Without cyclohexene in the feed, the conversion was constant at 100 % and the gum content remained almost constant with TOS. To incorporate the difference in conversion between the tests, Figure 7.5 also shows the dimer selectivity versus TOS. Although the dimer yield was lower in the 4-methylstyrene + cyclohexene test compared to the 4-methylstyrene test, the selectivity was almost the same after 21 days TOS and slightly higher after 30 days TOS.

Overall, the main impact of the addition of 20 wt% cyclohexene to 4-methylstyrene feed was a reduction in the 4-methylstyrene hydrogenation. This resulted in the availability of a higher concentration of 4-methylstyrene for dimerization and gum formation, compared to the case of no cyclohexene in the feed. This in turns resulted in catalyst deactivation.
Figure 7.5 Conversion, gum content dimers yield and selectivity with and without cyclohexene addition (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene (if indicated) in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Table 7.6 Product yields and conversions for 4-methylstyrene reaction with cyclohexene addition (Feed: 8.4 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TOS, days</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>1,4-di-(4'-methylphenyl)butane</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
</tr>
<tr>
<td>Total dimers selectivity, wt%</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>4-methylstyrene conversion, %</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Cyclohexene conversion, %</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Gum content mg/100 mL</td>
<td></td>
<td>125 ± 2</td>
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<tr>
<td>Bromine number, g / 100 g</td>
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<td>47.5 ± 1.6</td>
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<tr>
<td>Diene value, g I₂ / 100 g</td>
<td></td>
<td>6.8 ± 0.9</td>
</tr>
</tbody>
</table>
7.3 Temperature effect

To examine the effect of operating at a temperature lower than 250°C, the reaction was performed at 200°C using 8.4 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin. The results are summarized in Table 7.7. To compare the results at 200°C and 250°C, Figure 7.6 shows the conversion, gum content, dimers yield and selectivity at both temperatures. From this figure, a faster decrease in conversion was observed at 200°C, from 100 to 70.4 ± 2.5 %, compared to 250°C with conversion decreasing from 100 to 75.3 ± 2.7 %, after 30 days TOS. This change in conversion was accompanied by a lower yield and selectivity of hydrogenated products, higher yield and selectivity of dimers and higher gum content at 200°C versus 250°C reaction temperature. This indicates that the availability of a higher concentration of 4-methylstyrene at the lower temperature enhanced dimerization and gum formation and therefore resulted in catalyst deactivation.

This result is different from the results obtained with isoprene as described in Section 5.1, as slightly more dimers were formed at 250°C compared to 200°C in the case of isoprene. The difference can be attributed to the role of catalyst deactivation, which was more severe at 200°C versus 250°C in the case of 4-methylstyrene + cyclohexene and did not occur in the case of isoprene. The loss in catalyst activity can be attributed to the lower 4-methylstyrene conversion at 200°C versus 250°C, leaving higher concentration of 4-methylstyrene to dimerize and form gum that deposits on the catalyst causing catalyst deactivation.
Table 7.7 Product yields and conversions for 4-methylstyrene reaction with cyclohexene addition (Feed: 8.4 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin, T=200°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
<th>TOS, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td><img src="image1" alt="Structure" /></td>
<td>-</td>
<td>82.8 ± 2.9</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td><img src="image2" alt="Structure" /></td>
<td>-</td>
<td>6.6 ± 0.2</td>
</tr>
<tr>
<td>1,3-di-(4'-methylpheyl)butane</td>
<td><img src="image3" alt="Structure" /></td>
<td>-</td>
<td>10.7 ± 0.4</td>
</tr>
<tr>
<td>Total dimers selectivity, wt%</td>
<td>-</td>
<td>10.7 ± 0.4</td>
<td>29.4 ± 1.0</td>
</tr>
<tr>
<td>4-methylstylene conversion, %</td>
<td>-</td>
<td>100</td>
<td>93.2 ± 3.3</td>
</tr>
<tr>
<td>Cyclohexene conversion, %</td>
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<td>85.1 ± 3.0</td>
<td>44.6 ± 1.6</td>
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<tr>
<td>Gum content mg/100 mL</td>
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<td>78 ± 1</td>
<td>1681 ± 23</td>
</tr>
<tr>
<td>Bromine number, g / 100 g</td>
<td></td>
<td>47.5 ± 1.6</td>
<td>5.4 ± 0.2</td>
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</table>
Figure 7.6 Conversions, gum contents, product yields and selectivities at T=200 and 250°C (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
7.4 The effect of 4-methylstyrene content

To investigate the effect of 4-methylstyrene content on catalyst deactivation and reactor fouling, a feed consisting of 4.2 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin was hydrotreated at operating conditions relevant to the industrial hydrotreating process (T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The 4-methylstyrene content corresponds to a diene value of 9 g I₂ / 100 g, the diene value of the industrial naphtha feed. Table 7.8 lists the product yields, conversions, gum content and bromine number results. These results can be compared with the results listed in Table 7.6. To highlight the differences, Figure 7.7 compares the conversions, gum contents, 4-methylstyrene hydrogenated products/dimers yields and selectivities. From this figure, although the conversions were the same at 3 days TOS, the overall 4-methylstyrene conversion remained at 100% until 21 days TOS with 4.2 wt% 4-methylstyrene content and then decreased to 93.8 ± 3.3%. On the other hand, with 8.4 wt% 4-methylstyrene, the results show a faster decrease in conversion reaching 75.3 ± 2.7% at 30 days TOS. This indicates lower loss of overall catalyst activity with lower 4-methylstyrene content in the feed. The lower catalyst deactivation resulted in higher yields and selectivities of hydrogenated products which remained above 80 wt% after 30 days TOS in the case of the 4.2 wt% 4-methylstyrene compared to yields and selectivities below 60 wt% with 8.4 wt% 4-methylstyrene. With regards to dimers, higher yields and selectivities were obtained for the 8.4 wt% versus 4.2 wt% 4-methylstyrene following the same trend as the loss in catalyst activity indicated by the conversion results. The gum formation was the most sensitive to 4-methylstyrene content and increased more than 5 fold when the conjugated olefin content in the feed doubled.
Once again, these results indicate that catalyst deactivation occurred when higher concentration of 4-methylstyrene was present, resulting in higher dimerization activity. The loss of catalyst activity is also shown by the decrease in cyclohexene hydrogenation activity, as reflected in the cyclohexene conversion to cyclohexane, which was more severe when 8.4 wt% 4-methylstyrene was used versus 4.2 wt% as shown in Tables 7.6 and 7.8, respectively. The loss of hydrogenation activity is also indicated by the increase in bromine number which was more dramatic for 8.4 wt% versus 4.2 wt% 4-methylstyrene feeds.

The results from 4-methylstyrene experiments agree with the result obtained for isoprene in Section 5.2 which showed lower hydrogenation activity, higher dimerization activity, and higher gum formation with increasing conjugated olefin content in the feed.

### 7.5 Relationship between dimer formation, catalyst deactivation and reactor fouling

In the previous sections of this chapter, experiments were performed using 4-methylstyrene or α-methylstyrene with and without cyclohexene diluted in decalin as the reactor feed. The experiments were performed over a period of 30 days with liquid products collected every 24 hours. The products collected at 3, 12, 21 and 30 days TOS were analyzed using GC-MS to determine the feed conversions and product yields. Additional ASTM methods were performed on the products to obtain the gum content and the bromine number. After 3, 12, and 21 days the catalyst was recovered for analysis. This allows the investigation of catalyst properties with TOS.
Table 7.8 Product yields, conversions, gum contents and bromine numbers for 4-methylstyrene reaction with cyclohexene addition (Feed: 4.2 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Product</th>
<th>Structure</th>
<th>Yield, wt%</th>
<th>TOS, days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td><img src="structure1.png" alt="Structure" /></td>
<td>-</td>
<td>86.0 ± 3.0</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td><img src="structure2.png" alt="Structure" /></td>
<td>-</td>
<td>12.4 ± 0.4</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td><img src="structure3.png" alt="Structure" /></td>
<td>-</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>1,4-di-(4'-methylphenyl)butane</td>
<td><img src="structure4.png" alt="Structure" /></td>
<td>-</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Total dimers selectivity, wt%</td>
<td>-</td>
<td>1.5 ± 0.1</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>4-methylstyrene conversion, %</td>
<td>-</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cyclohexene conversion, %</td>
<td>-</td>
<td>98.5 ± 1.5</td>
<td>91.7 ± 3.2</td>
</tr>
<tr>
<td>Gum content mg/100 mL</td>
<td>-</td>
<td>61 ± 1</td>
<td>186 ± 2</td>
</tr>
<tr>
<td>Bromine number, g / 100 g</td>
<td>-</td>
<td>47.5 ± 1.6</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>
Figure 7.7 Conversions, gum contents, product yields and selectivities (Feed: 4.2 or 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/ feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
To investigate the relationship between dimer formation and gum production, Figure 7.8 shows the dimer yield versus gum yield of the liquid product for all experiments completed in the previous sections. From the figure, the overall trend shows an increasing gum yield in the liquid product with increasing dimer yield. In other words, the dimers seem to be a precursor for gum formation with higher concentration of gum formed in the presence of more dimers.

Figure 7.8 Gum content versus 4-methylstyrene dimers yield (Feed diluted in decalin, T=250°C unless indicated, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
To relate the dimer formation and gum formation to reactor fouling indicated by pressure drop across the reactor, Figure 7.9 compares the average pressure drop for 4- and α-methylstyrene reactions as a function of TOS. As shown in the figure, the reaction with 4-methylstyrene caused a pressure drop that increased with TOS, correlating with high dimer yield and gum formation. On the other hand, no pressure drop was detected for α-methylstyrene which produced very low yield of dimers (< 2 wt%) and gum (< 40 mg/100 mL). The pressure drop across the reactor is assumed to be caused by the deposition of gum on the reactor bed, decreasing the average reactor bed voidage. Consequently, with higher gum content, more gum deposits on the catalyst bed causing higher pressure drop which was detected with increasing TOS. Note that for 4-methylstyrene, the slight decrease in average pressure drop, which can be seen clearly after 17 days TOS, could be caused by the removal of part of the gum formed in the bed by the flowing liquid.

To support the assumption, the catalyst was recovered after 3, 12, and 21 days TOS to be characterized and compared with the catalyst properties with 30 days TOS. Tables 7.9, 7.10, and 7.11 list the measured catalyst properties. The data show an overall increase in carbon content and decrease in BET surface area of the catalyst compared to the catalyst properties at the start of the experiments (TOS = 0 days). However, no specific trend can be detected for carbon content and BET surface area with increasing TOS. This can be attributed to the difficulty in catalyst sampling. It is expected that the deposition of gum varies with bed height resulting in variability in carbon deposition. When the catalyst was recovered from the reactor, it was very difficult to sample different bed heights and the catalyst was instead randomly selected. In addition, gum
formation was detected on other parts of the bed, i.e. on the glass beads and silicon carbide, but due to the very small quantity, it was difficult to recover and quantify.

Figure 7.9 Average pressure drop across reactor versus TOS (Feed: 8.4 wt% 4- or α-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

However, from Table 7.9, comparing the catalyst recovered from the experiments with 4- and α-methylstyrene, which showed a significant difference in dimerization activity, shows that the decrease in BET surface and the increase in carbon content was larger for 4-methylstyrene versus α-methylstyrene, in agreement with the higher dimer formation and gum content results from 4-methylstyrne versus α-methylstyrene. Also from Table 7.10, comparing 4-methylstyrene+cyclohexene, reacted at 200 and 250°C, the BET surface area was smaller and the
carbon content was higher at 200 versus 250°C after 30 days TOS, which corresponds to the higher dimer yields and gum content measured for the reaction completed at 200 versus 250°C, as shown in Figure 7.6.

Based on our assumption of pressure drop change being caused by change in average reactor bed voidage, the following equations were used to estimate the required change in average reactor bed voidage to achieve the measured pressure drop [66]:

\[
\log_{10} \left( \frac{P_{lg}}{P_l + P_g} \right) = \frac{0.416}{\log_{10} \left( \frac{P_l}{P_g} \right)^{1/2} + 0.666}
\]

\[
\frac{\Delta P}{L_b} = \frac{U(1 - \varepsilon_b)}{\phi_p D_p \varepsilon_b} \left[ \frac{150 \mu(1 - \varepsilon_b)}{\phi_p D_p} + 1.75 \rho U \right]
\]

where,

- \( P_{lg} \) = two phase pressure drop across bed, kPa.
- \( P_l \) = single phase pressure drop across bed for the liquid flowing alone, kPa.
- \( P_g \) = single phase pressure drop across bed for the gas flowing alone, kPa.
- \( \Delta P \) = single phase pressure drop across bed, kPa.
- \( L_b \) = bed height, m.
- \( U \) = fluid superficial velocity, m/s.
\( \varepsilon_b = \text{Average reactor bed voidage, dimensionless} = \left( \sum \frac{W_i}{\varepsilon_i} \right)^{-1}. \)

\( w_i = \text{mass fraction of particle, wt \%}. \)

\( \varepsilon_i = \text{bed voidage of particle } i, \text{ dimensionless} \) (0.466 for catalyst [77], 0.4 for SiC and 0.3 for glass beads [78]).

\( \phi_p = \text{particle sphericity, dimensionless}. \)

\( \bar{D}_p = \text{average particle diameter, m} = \left( \sum \frac{W_i}{D_{p,i}} \right)^{-1}. \)

\( D_{p,i} = \text{diameter of particle } i, \text{ m} \)

\( \rho = \text{fluid density, kg/m}^3. \)

\( \mu = \text{fluid viscosity, kPa} \cdot \text{s}. \)
Table 7.9 Carbon content and BET surface area of Ni-Mo-S/γ-Al₂O₃ before and after reactions (Feed: 8.4 wt% 4- or α-methylstyrene (+ 20 wt% cyclohexene, if indicated) in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Feed</th>
<th>α-methylstyrene</th>
<th>4-methylstyrene</th>
<th>4-methylstyrene +cyclohexene</th>
<th>α-methylstyrene</th>
<th>4-methylstyrene</th>
<th>4-methylstyrene +cyclohexene</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOS, days</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>11.7±0.1*</td>
<td></td>
<td></td>
<td>156 ± 6</td>
</tr>
<tr>
<td>3</td>
<td>11.1±2.2</td>
<td>13.9±0.7</td>
<td>17.3±1.3</td>
<td>125 ± 5</td>
<td>97 ± 4</td>
<td>94 ± 4</td>
</tr>
<tr>
<td>7</td>
<td>14.7±1.3</td>
<td>-</td>
<td>-</td>
<td>120 ± 5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>17.7±0.4</td>
<td>17.8±0.8</td>
<td>-</td>
<td>110 ± 1</td>
<td>92 ± 4</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>18.3±0.8</td>
<td>19.6±1.6</td>
<td>-</td>
<td>92 ± 4</td>
<td>80 ± 3</td>
</tr>
<tr>
<td>30</td>
<td>15.1±0.8</td>
<td>17.4 ± 0.5</td>
<td>17.9±0.4</td>
<td>113 ± 5</td>
<td>94 ± 4</td>
<td>82 ± 3</td>
</tr>
</tbody>
</table>

*Standard error. Refer to Appendix C for details.
Table 7.10 Carbon content and BET surface area of Ni-Mo-S/γ-Al₂O₃ after 30 days TOS (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Used catalyst properties</th>
<th>Reaction temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Carbon content, wt%</td>
<td>18.5 ± 0.6*</td>
</tr>
<tr>
<td>BET surface area, m²/g</td>
<td>66 ± 3</td>
</tr>
</tbody>
</table>

*Standard error. Refer to Appendix C for details

Table 7.11 Carbon content and BET surface area of Ni-Mo-S/γ-Al₂O₃ after 30 days TOS (Feed: 4-methylstyrene + 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Used catalyst properties</th>
<th>4-methylstyrene content in feed, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td>Carbon content, wt%</td>
<td>24.3 ± 4.4*</td>
</tr>
<tr>
<td>BET surface area, m²/g</td>
<td>76 ± 3</td>
</tr>
</tbody>
</table>

*Standard error. Refer to Appendix C for details

Figure 7.10 shows the model fit versus measured pressure drop obtained by varying the average reactor bed voidage as a model parameter, for 4-methylstyrene + cyclohexene reactions (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). Based on the model, the average reactor bed voidage decreased from 0.39 to 0.12.
The large decrease in average reactor bed voidage was visually noticed after reactor shutdown as the bed was plugged with gum and unloading of the bed was not possible without using external force. Assuming the decrease in reactor bed voidage is caused by cumulative gum deposition, this corresponds to a gum content of 221 mg/100 mL, a reasonable value that supports the possibility of pressure drop caused by gum deposition given that the measured gum content in the liquid product reached 2469 ± 33 mg/100 mL at 30 days TOS for 4-methylstyrene + cyclohexene reaction (refer to Appendix B for detailed calculations).

Figure 7.10 Measured pressure drop versus TOS compared to calculated pressure drop versus average reactor bed voidage (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
7.6 Summary

This chapter investigated the role of dimerization reactions in catalyst deactivation and reactor fouling. The tests were completed over periods of 3, 12, 21, and 30 days TOS at the same industrially relevant process conditions (T = 200-250°C, P = 3.4 MPa, LHSV = 2 hr⁻¹, H₂/feed = 392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃) with the catalyst recovered and characterized after each TOS period of 3, 12, 21 and 30 days.

The effect of steric hindrance was studied by comparing 4- and α-methylstyrene hydrogenation. It was shown that the steric hindrance, provided by the methyl group attached to the vinyl group, caused a significant decrease in dimerization activity while the hydrogenation activity remained high. This group limits access to and reactivity with the double bonds and therefore less oligomers are formed.

The addition of 20 wt% cyclohexene to 4-methylstyrene resulted in a significant loss in hydrogenation activity while the dimerization activity remained almost the same. The loss of catalyst activity can be attributed to the availability of a higher concentration of 4-methylstyrene for dimerization and gum formation when the overall conversion is lower. This in turn resulted in increased catalyst deactivation compared to the case with no cyclohexene in the feed.

The effect of operating at a lower temperature was also investigated by reacting 8.4 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin at 200°C. A faster decrease in conversion was detected at 200°C versus 250°C, accompanied by lower yield/selectivity of hydrogenated products and higher yield/selectivity of dimers and gum content. This was attributed to
availability of a higher concentration of 4-methylstyrene at the lower temperature which enhanced dimerization and gum formation and therefore resulted in faster catalyst deactivation.

To investigate the effect of conjugated olefin content, an experiment with 4.2 wt% 4-methylstyrene + 20 wt% cyclohexene was completed. The conversion was more stable and stayed at 100% for 21 days TOS and ended with 93.8 ± 3.3% after 30 days TOS, indicating slower catalyst deactivation than with 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene which resulted in a conversion of 75.3 ± 2.7 wt% at 30 days TOS. This was accompanied by higher yields/selectivities of hydrogenated products and lower yields/selectivities of dimers which stayed > 80 wt% and < 14 wt% versus < 60 wt% and > 25 wt% after 30 days TOS for 4.2 wt% and 8.4 wt % 4-methylstyrene, respectively. The gum formation showed the highest sensitivity to conjugated olefin content and increased more than 5 fold when the 4-methylstyrene content in the feed doubled.

Plotting dimer yield versus gum yield for all experiments showed an overall trend of increasing gum yield with increasing dimer yield. This suggests that the dimers are precursors for gum formation.

To investigate the link between reactor fouling, dimer formation and gum formation, the pressure drop across the reactor for 4- and α-methylstyrene reactions was examined. 4-methylstyrene reactions resulted in a pressure drop that increased with TOS compared to no change in pressure for α-methylstyrene reactions. This correlated with higher dimerization activity and gum formation, respectively, which supports the assumption that the increase in pressure drop was
caused by cumulative gum deposition in the catalyst bed, decreasing the average reactor bed voidage.

The catalyst characterization results showed an overall increase in carbon content and decrease in BET surface area after reaction. The catalysts analyzed after reactions of 4- and α-methylstyrene, showed larger carbon deposition and larger decrease in BET surface area, in agreement with the higher dimerization activity and gum content, respectively. The same agreement was obtained for 4-methylstyrene + cyclohexene reacted at 200 and 250°C. Consequently, catalyst deactivation can be linked to carbon deposition on the catalyst caused by dimer and gum formation.

Finally, using the Ergun equation, it was found that 221 mg of gum/100 mL of liquid needs to be deposited in the catalyst bed to achieve the measured change in pressure drop for 4-methylstyrene + cyclohexene reaction. This value is reasonable given that the measured gum content in the liquid product reached 2469 ± 33 mg/100 mL at 30 days TOS stream and supports the assumption of reactor fouling resulting from a decreasing average reactor bed voidage caused by cumulative gum deposition.
Chapter 8: Kinetic investigation of 4-methylstyrene hydrogenation and dimerization

This chapter examines the reaction kinetics of 4-methylstyrene hydrogenation and dimerization over spent commercial Ni-Mo-S/γ-Al₂O₃ obtained from Syncrude after hydrotreater shutdown. To estimate the kinetic parameters, experiments were conducted using 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin for a duration of 3 days TOS, each at 4 different temperatures, 150, 180, 200, and 250°C, and 3 different LHSV, 2, 4, and 8 h⁻¹. The feed 4-methylstyrene content corresponds to a diene value of 18 g I₂ / 100 g, double the diene value in a typical naphtha feed [13], to increase the degree of dimerization and aid the detection and quantification of products for better kinetic parameter estimation. Other reaction conditions were maintained at industrially relevant process conditions (P=3.4 MPa, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃). The purpose of estimating the kinetic parameters is to provide a means of predicting hydrogenation and dimerization activity during industrial hydrotreating reactions, to aid in identifying process conditions to improve hydrogenation yield while minimizing dimerization yield.

8.1 Reaction steps for kinetic parameter estimation

In order to estimate the reaction constants and activation energies, reaction steps must be proposed. Based on the GC-MS analysis of products, hydrotreating 8.4 wt% 4-methylstyrene (4-MS) + 20 wt% cyclohexene (cC₆=) in decalin at industrially relevant process conditions (T=150-250°C, P=3.4 MPa, LHSV=2-8 h⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-
Al₂O₃) produced 4-MS hydrogenated products, namely 1-ethyl-4-methylbenzene and 1-ethyl-4-methylcyclohexane, and 4-MS dimers namely, 1,3-di-(4'-methylphenyl)butane and 1,3-di-(4'-methylphenyl)butane. The only product detected from cyclohexene (cC₆=) was cyclohexane (cC₆). To improve the kinetic parameter estimation, the number of estimated parameters was reduced by lumping 4-MS hydrogenated products and 4-MS dimerization products. Hence the following reaction steps are proposed for the kinetic parameter estimation:

1) Hydrogenation (4-MS):

\[ \text{Hydrogenated products (HYD)} \]

[Diagram of hydrogenation reaction]

\[ k_1 \text{H}_2 \]

2) Dimerization (4-MS):

\[ \text{Dimers (C18)} \]

[Diagram of dimerization reaction]
3) Hydrogenation (cC6=):

\[
\begin{align*}
\text{Using the power law model, the reaction rates can be expressed as follows:} \\
\dot{r}_1 &= k_1 \cdot C_{4-MS} \\
\dot{r}_2 &= k_2 \cdot (C_{4-MS})^2 \\
\dot{r}_3 &= k_3 \cdot C_{cC6=} 
\end{align*}
\]

where,

\[
\dot{r}_j = \text{rate of reaction } j \text{ in terms of catalyst mass, mol/(g·h)}. \\
k_j = \text{reaction constant for reaction } j = k_j / (\rho_{\text{cat}} \cdot (1 - \varepsilon_{\text{cat}})), \text{ L/(g·h) for } j = 1, 3, \text{ and L}^2/(\text{mol·g·h}) \text{ for } j = 2. \\
k_j = \text{reaction rate constant for reaction } j, \text{ h}^{-1} \text{ for } j = 1, 3 \text{ and L/(mol·h) for } j = 2. \\
\rho_{\text{cat}} = \text{catalyst density, g/L}. \\
\varepsilon_{\text{cat}} = \text{catalyst bed voidage = 0.466 for trilobe pellets, dimensionless [77].} \\
C_i = \text{concentration of chemical species } i, \text{ mol/L}. 
\]
8.2 Mole balance derivation

Referring to the packed bed reactor schematic in Figure 8.1, the general mole balance equation can be written as follows:

\[
F_i(W) - F_i(W + \Delta W) + \Delta W \sum_{j=1}^{N_k} v_{ji} \Omega_j a_j r'_j = \frac{dN_i}{dt}
\]  

(8.7)

where

\( F_i = \) molar flow of species \( i \), mol/h.

\( W = \) catalyst mass, g.

\( v_{ji} = \) stoichiometric coefficient of species \( i \) in reaction \( j \), dimensionless.

\( \Omega_j = \) overall effectiveness factor of reaction \( j \), dimensionless.

\( a_j = \) catalyst activity factor of reaction \( j \), dimensionless.

\( N_i = \) number of moles of species \( i \), mol

\( t = \) time, h.

Figure 8.1 Packed bed reactor schematic.
Assuming steady state operation, \( \frac{dN_i}{dt} = 0 \) (no molar accumulation).

Dividing by \( \Delta W \) and taking the limit as \( \Delta W \to 0 \), the following equation is obtained:

\[
- \frac{dF_i}{dW} + \sum_{j=1}^{N_k} \nu_j \Omega_j a_j r_j = 0
\] (8.8)

The following assumptions are made,

- No catalyst deactivation during the short reaction duration of 3 days; i.e. \( a_j = 1 \).

- Negligible external and internal mass transfer effects, \( \Omega_j = 1 \) (refer to Appendix D for detailed calculations).

The mole balance equation reduces to the following:

\[
\frac{dF_i}{dW} = \sum_{j=1}^{N_k} \nu_j r_j
\] (8.9)

Therefore, the mole balance for the reacting species can be written as following:

\[
\frac{dF_{4-MS}}{dW} = -r_1 - 2r_2
\] (8.10)

\[
\frac{dF_{HYD}}{dW} = r_1
\] (8.11)
\[
\frac{dF_{c18}}{dW} = r_2'
\]  
(8.12)

\[
\frac{dF_{cC6-}}{dW} = -r_3'.
\]  
(8.13)

Equations (8.10) to (8.13) can be written in terms of species concentrations as follows assuming negligible change in liquid volume:

\[
\frac{dC_{4-MS}}{dW} = \frac{-r_1' - 2r_2'}{v_0}
\]  
(8.14)

\[
\frac{dC_{HYD}}{dW} = \frac{r_1'}{v_0}
\]  
(8.15)

\[
\frac{dC_{c18}}{dW} = \frac{r_2'}{v_0}
\]  
(8.16)

\[
\frac{dC_{cC6-}}{dW} = \frac{-r_3'}{v_0}
\]  
(8.17)

where,

\[v_0 = \text{volumetric flow rate of the feed, L/h.}\]
8.3 Kinetic parameter estimation

The parameter estimation was achieved by minimizing the objective function using the sum of least squares method. The objective function was defined as the sum of squares of the difference between experimentally measured and model calculated concentrations for all reacting species \( i \) at all catalyst weights, \( W \), as follows:

\[
OBJ = \sum_t \sum_i \left( C_{\text{exp},i,W} - C_{\text{pred},i,W} \right)^2
\]  

(8.18)

The objective function was minimized using a Nelder-Mead simplex (direct search) method in MATLAB R2011a version 7.12.0. At each iteration, the ordinary differential equations (8.14), and (8.15), together with the component mole balance equation, were solved simultaneously using the Runge-Kutta method to predict the concentrations of the reacting species required by the objective function. The kinetic parameter estimation of cyclohexene reaction was completed in the same manner independently by solving Equation (8.17) to predict the concentration of cyclohexene required for the objective function. The initial conditions used were as follows:

\[
C_{4-MS} = 6.24\text{E}-1 \text{ M}, \quad C_{\text{HYD}} = 0 \text{ M}, \quad \text{and} \quad C_{\text{C6e}} = 2.14 \text{ M (at W=0)}.
\]

The full MATLAB code to solve the ordinary differential equations are included in Appendix H.

Table 8.1 shows the estimated rate constants for \( T=150-250^\circ\text{C} \) for day 2 and day 3 TOS. As expected, all the reaction rate constants increased with temperature reflecting the increase in reaction rates with temperature. Comparing \( k_1 \) with \( k_3 \) shows that the hydrogenation rate for 4-
methylstyrene was higher than that of cyclohexene at all temperatures tested. This is in agreement with previous studies that stated conjugated olefin/diolefin hydrogenation was always faster than mono-olefin hydrogenation as discussed in Section 2.2. Table 8.1 also shows that the dimerization rate constants were much smaller than the hydrogenation rate constants at all temperatures tested, indicating slower dimerization reaction rates.

Table 8.1 Estimated reaction rate constants (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>TOS, days</th>
<th>Temperature, °C</th>
<th>k₁, h⁻¹</th>
<th>k₂, L/(mol·h)</th>
<th>k₃, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>150</td>
<td>2.65 ± 0.03</td>
<td>0.09 ± 0.03</td>
<td>0.69 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>4.48 ± 0.08</td>
<td>0.77 ± 0.12</td>
<td>1.62 ± 0.41</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>5.91 ± 0.02</td>
<td>2.48 ± 0.03</td>
<td>1.44 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>13.07 ± 0.02</td>
<td>2.15 ± 0.03</td>
<td>3.89 ± 0.66</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>2.17 ± 0.02</td>
<td>0.24 ± 0.03</td>
<td>0.56 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>3.50 ± 0.02</td>
<td>0.97 ± 0.02</td>
<td>1.22 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.89 ± 0.04</td>
<td>1.79 ± 0.04</td>
<td>1.02 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>8.56 ± 0.01</td>
<td>1.28 ± 0.02</td>
<td>2.84 ± 0.59</td>
</tr>
</tbody>
</table>

Plots of the measured versus calculated concentrations as a function of catalyst weight at different temperatures are shown in Figure 8.2 and Figure 8.3 for 4-methylstyrene and cyclohexene reactions, respectively. The plots show the results estimated in day 2 and day 3 TOS. The degree of explanation ($R^2$) was calculated using Equation (8.14) and was found to be
0.96 and 0.96 for 4-methylstyrene reactions and 0.93 and 0.92 for cyclohexene reactions for day 2 and 3 TOS, respectively.

\[
R^2 = \frac{\sum_w \sum_i (C_{\exp,i,w} - C_{\text{pred},i,w})^2}{\sum_w \sum_i (C_{\exp,i,w} - \overline{C}_{\exp,w})^2}
\]

(8.14)

Using the Arrhenius equation (8.15), the activation energies were calculated from the slope by plotting \(\ln(k_j)\) versus 1/T. The plots are shown in Figure 8.4 and Figure 8.5. The activation energies are listed in Table 8.2.

\[
k_j = A_j \cdot \exp\left(\frac{-E_{\text{ai}}}{R \cdot T}\right)
\]

(8.15)

The activation energies obtained for 4-methylstyrene hydrogenation and dimerization are slightly lower than the values reported for \(\alpha\)-methylstyrene as shown previously in Section 2.5. The difference in reactivity can be attributed to the difference in the structure of the conjugated olefin and the catalyst used.

The activation energy quantifies the reaction barrier that reflects the production and consumption of chemical species. From the data of Table 8.2, the activation energy for the hydrogenation of 4-methylstyrene is slightly lower than that of cyclohexene. Both hydrogenation activation energies are much lower than that for the dimerization reaction. This reflects the higher yield of hydrogenated products obtained compared to dimer yields.
The estimated reaction constants were used to calculate the initial reaction rates for 4-methylstyrene hydrogenation and dimerization and the results are shown in Table 8.3. The relative rates were also calculated by dividing the rate of hydrogenation by the rate of dimerization of 4-methylstyrene. As seen in Table 8.3, the results indicate that the hydrogenation/dimerization rate ratio can be maximized to 48.96 by operating at T=150°C based on the results of day 2 TOS. At day 3 TOS, the estimated rate constants showed that operating at T=150°C and 250°C would result in the highest hydrogenation/dimerization rate ratio of 15.1 and 10.9, respectively. On the other hand, the lowest hydrogenation/dimerization rate ratio would be achieved by operating at T=200°C for both 2 and 3 days TOS. This can be explained by the effects of temperature and 4-methylstyrene concentration on the reaction rates. At 150°C, the hydrogenation rate of 4-methylstyrene is lowest leaving more 4-methylstyrene concentration to dimerization compared to other tested reaction temperatures. But due to the high activation energy of the dimerization reaction, not enough energy is available to overcome the dimerization reaction activation barrier and the hydrogenation/dimerization rate ratio remains high. As the temperature increases, more energy is available for the dimerization reaction to occur causing the dimerization rate to increase and the hydrogenation/dimerization rate ratio to decrease down to a minimum of 3.56 at 200°C. At 250°C, the hydrogenation rate of 4-methylstyrene is highest leaving less 4-methylstyrene concentration to dimerize and therefore the dimerization reaction rate decreases while the hydrogenation/dimerization rate ratio increases.
Figure 8.2 Measured and model predicted concentration for 4-methylstyrene reactions (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Figure 8.3 Measured and model predicted concentration for cyclohexene hydrogenation (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/Feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Figure 8.4 Arrhenius plot for 4-methylstyrene reactions (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

Figure 8.5 Arrhenius plot for cyclohexene hydrogenation (Feed: 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).
Table 8.2 Estimated activation energies for 4-methylstyrene and cyclohexene reactions (Feed: 8.4 wt% 4-ethylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>TOS, days</th>
<th>$E_{a1}$, kJ/mol</th>
<th>$E_{a2}$, kJ/mol</th>
<th>$E_{a3}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>29.3 ± 1.2</td>
<td>111.3 ± 2.6</td>
<td>30.2 ± 6.0</td>
</tr>
<tr>
<td>3</td>
<td>24.8 ± 2.7</td>
<td>68.2 ± 5.2</td>
<td>28.2 ± 6.4</td>
</tr>
</tbody>
</table>

Table 8.3 Initial 4-methylstyrene hydrogenation and dimerization reaction rates (Feed: 8.4 wt% 4-ethylstyrene + 20 wt% cyclohexene in decalin, T=150-250°C, P=3.4 MPa, LHSV=2-8 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>TOS, days</th>
<th>Temperature, °C</th>
<th>$r_1$, mol/(L·h)</th>
<th>$r_2$, mol/(L·h)</th>
<th>$r_1/r_2$ dimensionless</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>150</td>
<td>1.62</td>
<td>3.30E-2</td>
<td>48.96</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>2.73</td>
<td>2.86E-1</td>
<td>9.56</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.61</td>
<td>9.24E-1</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>7.97</td>
<td>8.00E-1</td>
<td>9.97</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>1.33</td>
<td>8.79E-2</td>
<td>15.07</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>2.13</td>
<td>3.59E-1</td>
<td>5.94</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.37</td>
<td>6.67E-1</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>5.22</td>
<td>4.77E-1</td>
<td>10.94</td>
</tr>
</tbody>
</table>
8.4 Summary

The reaction kinetics for 4-methylstyrene hydrogenation and dimerization and cyclohexene hydrogenation were investigated. 12 experimental runs were completed, with a duration of 3 days on stream for each, using 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin at 4 different temperatures and 3 different LHSV ranging from 150 to 250°C, and 2 to 8 h⁻¹, respectively. Other reaction conditions were set at the same industrially relevant process conditions used previously (P=3.4 MPa, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

The parameters were estimated by minimizing the objective function using the sum of least squares method. The minimization was achieved using Nelder-Mead simplex (direct search) method in MATLAB.

The estimated rate constants showed that the hydrogenation rate for 4-methylstyrene was higher than that of cyclohexene at all temperatures tested. The dimerization rate constants were found to be much smaller than the hydrogenation rate constants at all temperatures tested, indicating slower dimerization reaction rates.

Using the Arrhenius equation, the activation energies were obtained and the values were found to be slightly lower than the literature reported values for α-methylstyrene. This can be explained by the difference in conjugated olefin structure and the catalyst used. The activation energy for the hydrogenation of 4-methylstyrene was found to be slightly lower than that of cyclohexene.
with both values much lower than that of the dimerization reaction. This was in agreement with the higher yield obtained for hydrogenated products compared to dimers.

The estimated reaction kinetics showed that operating at T=150°C and 250°C would result in the highest hydrogenation/dimerization rate ratio of 15.1 and 10.9, respectively. On the other hand, the lowest hydrogenation/dimerization rate ratio would be achieved by operating at T=200°C.
Chapter 9: Conclusions and recommendations

9.1 Conclusions

The aim of this study was to investigate the reactions of olefins/diolefins that lead to catalyst deactivation and fouling in naphtha hydrotreater reactors using commercial Ni-Mo-S/γ-Al₂O₃ catalyst. Two micro-scale fixed bed reactor systems were constructed and used for this study.

Initially, the onset of oligomerization reactions was examined using fresh and spent commercial Ni-Mo-S/γ-Al₂O₃. Significant dimer yields were detected when isoprene was used over spent Ni-Mo-S/γ-Al₂O₃ catalyst. This indicated oligomerization activity was not only linked to catalyst activity, but also to the structure of the diolefin as a high degree of dimerization and large decrease in catalyst activity were detected when isoprene, the less sterically hindered diolefin, was used instead of the more sterically hindered 2,5-dimethyl-2,4-hexadiene.

Due to its tendency to dimerize, isoprene was selected as a model diolefin to investigate the effect of process conditions, namely temperature and diolefin content, on dimerization activity and reactor fouling. As the reaction temperature increased, the hydrogenated products yield decreased while the total oligomer yield increased. The oligomers formed were mostly isoprene dimers. The increase in dimerization activity was explained by the higher activation energy for dimerization reactions compared to hydrogenation. As the isoprene content increased, the hydrogenation product yield decreased while the oligomerization activity increased. The higher increase in oligomerization reaction rate compared to that of hydrogenation, depicted by the
product yields, as the concentration of isoprene increased, suggested that the dimerization is of higher reaction order than hydrogenation.

The effect of the olefin/diolefin structure, comparing linear versus cyclic conjugation, and sterically hindered olefins/diolefins, on the oligomerization reactions was also examined. Conjugation was shown to play an important role in oligomerization. The resonance generated by conjugation aids in stabilizing the formed allylic carbocation due to π-electron delocalization and positive charge spreading to reduce the electron deficiency. The proposed allylic carbocation formation is a key step in dimerization and oligomerization reactions. The effect of cyclic diolefin concentration was investigated and it was found that a larger increase in oligomer formation was detected compared to hydrogenated products yield when the concentration of the diolefin in the feed increased. Again, this indicated that the order of the oligomerization reaction rate is higher than that of hydrogenation. Steric hindrance was also shown to play a role in limiting the degree of oligomerization as it limits access to and reactivity of the double bonds.

The experiments performed with 4-methylstyrene showed that this conjugated olefin gave the highest oligomer yield compared to all other olefins/diolefins tested. This was explained by the higher stabilization of the allylic carbocation formed compared to other olefins/diolefins tested due to the delocalization of the π-electron and the spread of the positive charge among more carbon atoms.

The catalyst deactivation and reactor fouling that results from the dimerization of conjugated olefins during hydrotreating reactions was then investigated. The tests were completed over periods of 3, 12, 21, and 30 days time-on-stream (TOS) at the same process conditions (T =200-
250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃) with the catalyst recovered and characterized after each test. The effect of steric hindrance was studied by comparing 4- and α-methylstyrene hydrogenation. It was shown that the steric hindrance, provided by the methyl group attached to the vinyl group, caused a significant decrease in dimerization activity while the hydrogenation activity remained high.

The addition of 20 wt% cyclohexene to 4-methylstyrene feed resulted in a significant loss in hydrogenation activity while the dimerization activity remained almost the same. The loss of catalyst activity was attributed to the availability of a higher concentration of 4-methylstyrene for dimerization and gum formation when the overall conversion is lower. This in turn resulted in increased catalyst deactivation compared to the case with no cyclohexene in the feed.

The effect of operating at a lower temperature was also investigated by reacting 8.4 wt% 4-methylstyrene and 20 wt% cyclohexene in decalin at 200°C. Faster decrease in conversion versus TOS was detected at 200°C versus 250°C, accompanied by lower yield/selectivity of hydrogenated products and higher yield/selectivity of dimers and gum content. This was attributed to the availability of a higher concentration of 4-methylstyrene at the lower temperature, which enhanced dimerization and gum formation and therefore resulted in faster catalyst deactivation.

To investigate the effect of conjugated olefin content, an experiment with 4.2 wt% 4-methylstyrene + 20 wt% cyclohexene was completed. The conversion was more stable versus TOS indicating slower catalyst deactivation than with 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene. This was accompanied by higher yields/selectivities of hydrogenated products and
lower yields/selectivities of dimers. The gum formation showed the highest sensitivity to conjugated olefin content and increased more than 5 fold when the 4-methylstyrene content in the feed doubled.

Plotting dimer yield versus gum yield showed an overall trend of increasing gum yield with increasing dimer yield. This suggests that the dimers are precursors for gum formation.

To investigate the link between reactor fouling, dimer formation and gum formation, the pressure drop across the reactor for 4- and α-methylstyrene reactions was examined. 4-methylstyrene reactions resulted in a pressure drop that increased with TOS compared to no change in pressure for α-methylstyrene reactions. This correlated with higher dimerization activity and gum formation, respectively, which supports the assumption that the increase in pressure drop is caused by cumulative gum deposition in the catalyst bed, decreasing the average reactor bed voidage.

Using the Ergun equation, it was found that 221 mg of gum/100 mL of liquid needs to be deposited in the catalyst bed to achieve the measured change in pressure drop for 4-methylstyrene+cyclohexene reaction. This value is reasonable given that the measured gum content in the liquid product reached 2469 mg/100 mL at 30 days TOS stream and supports the assumption of reactor fouling resulting from decreasing average reactor bed voidage caused by cumulative gum deposition.

A kinetic model of the hydrogenation and dimerization of 4-methylstyrene over spent commercial Ni-Mo-S/γ-Al₂O₃ showed that hydrogenation has much lower activation energy
(24.8 kJ/mol) than dimerization (68.2 kJ/mol). The estimated reaction kinetics also showed that operating at T=150°C and 250°C would result in the highest hydrogenation/dimerization rate ratio of 15.1 and 10.9, respectively. On the other hand, the lowest hydrogenation/dimerization rate ratio would be achieved by operating at T=200°C.

9.2 Recommendations

9.2.1 Effect of catalyst properties

The focus of the current study was on investigating dimerization activity during hydrogenation over commercial Ni-Mo-S/γ-Al2O3 catalyst. The study proposed that dimerization was initiated by the formation of allylic carbocation by reaction with a Bronsted acid. This proposal can be confirmed by controlling the acidity of the catalyst by preparing a new catalyst supported on aluminosilicate and changing the (Si/Si+Al) ratio. In addition, it is recommended to investigate the effect of MoS2 structure on dimerization activity. The MoS2 structure, specifically stacking height and particle size, can be varied by changing the loading of MoS2 and calcination temperature.

9.2.2 Using a more realistic feed

Bitumen-derived naphtha contains a mixture paraffins, isoparaffins, aromatics, naphthenes and olefins/diolefins. In the current study, the focus was to understand the process of olefin/diolefin dimerization/oligomerization and therefore a model olefin/diolefin was diluted with decalin to allow for product identification using GC-MS analysis. However, to better mimic the industrial
process, it is recommended to hydrotreat a feed consisting of a mixture of olefins/diolefins diluted in HTGO.

9.2.3 Effect of other olefin structures on dimerization activity

This study showed that the addition of 1-octene, a linear olefin, did not contribute to the dimerization. On the other hand, the addition of a cyclic olefin, cyclohexene, enhanced dimerization activity by decreasing the overall catalyst activity. This showed that olefin structure plays an important role in dimerization activity. Therefore, it is recommended to investigate other olefin structures such sterically hindered olefins or polycyclic olefins.

9.2.4 Effect of other process conditions

In this study, the effect of temperature, olefin/diolefin content and mono-olefin addition was mainly investigated on the dimerization/oligomerization activity. Other process conditions, such as pressure, H₂/feed ratio, might also play a role in dimerization activity. Therefore, it is recommended to study the effect of these other conditions on the dimerization activity during olefin/diolefin hydrogenation.

9.2.5 Langmuir-Hinshelwood model for kinetic parameter estimation

Although the power law kinetic model estimated the kinetic parameters with high degree of explanation ($R^2$) of 0.96, using a Langmuir-Hinshelwood kinetic model takes into account adsorption, desorption and surface reaction and therefore describe the reaction better.
mechanistically. In addition, Langmuir-Hinshelwood kinetic model quantifies the adsorption/desorption of the mono-olefin and the conjugated olefin/diolefin and therefore any competitiveness would be determined.
Bibliography


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13. S. Yui, Removing diolefins from coker naphtha necessary before hydrotreating., Oil & Gas Journal 97 (1999) 64, 66-68.


73. UOP 326-08, Diene value by maleic anhydride addition reaction (2006).


Appendices
Appendix A  Thermal dimerization of 4-methylstyrene

To compare the degree of thermal versus catalytic dimerization activities, a feed consisting of 8.4 wt% in decalin was hydrotreated at operating conditions relevant to the industrial hydrotreating process (T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL), replacing the catalyst with SiC (mesh#80). Table A.1 lists the 4-methylstyrene conversions, dimer yields, and dimer/4-methylstyrene yield ratio. For thermal hydrogenation, 4-methylstyrene was mainly converted to octahydro-1H-indene. Less than 1 wt% of 1-ethyl-4-methylcyclohexane was detected. On the other hand, for catalytic hydrogenation, the main products were 1-ethyl-4-methylbenzene and 1-ethyl-3-methylcyclohexane with 28.9 w% and 7.6 wt%, respectively. As shown in the table, the catalytic dimerization yield was much higher than that of thermal even though the concentration of 4-methylstyrene available of dimerization was lower as reflected by the higher conversion of 4-methylstyrene. To make the results more comparable, the dimerization activity was normalized with 4-methylstyrene concentration by dividing the dimer yield by the 4-methylstyrene yield. The ratio is shown in Table A.1. The dimer/4-methylstyrene yield ratio from catalytic reactions was 10-13 times higher than that from thermal reaction. These results suggest that dimerization is mainly catalytic. This was further confirmed by the results obtained from the kinetic study, reported earlier in Chapter 8, which indicated that dimerization activity correlated with the catalyst amount used.
Table A.1 Comparison between thermal and catalytic dimerization activity (4-methylstyrene content=8.4 wt%, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th></th>
<th>Thermal</th>
<th>Catalytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>250°C</td>
<td>200°C</td>
</tr>
<tr>
<td>4-methylstyrene conversion, %</td>
<td>43.9</td>
<td>70.4</td>
</tr>
<tr>
<td>Dimer yield, wt%</td>
<td>5.2</td>
<td>37.1</td>
</tr>
<tr>
<td>Dimer/4-methylstyrene yield ratio</td>
<td>0.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Appendix B  Sample calculations

B.1  Conversion, yield, selectivity and concentration calculations from GC-MS data

In this section, sample calculations of the feed conversion, product yields, selectivities and concentrations from GC-MS areas are shown. The product sample discussed was collected after 1 day TOS of the hydrogenation of 8.4 wt% 4-methylstyrene + 20 wt% cyclohexene in decalin (T =150°C, P=3.4 MPa, LHSV=8 hr^{-1}, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

A product sample was diluted for GC-MS analysis as outlined in Section F.1. The preparation data are shown in Table B.1. The GC-MS analysis results of these samples are shown in Table B.2.

**Table B.1 Product sample dilution for GC-MS analysis.**

<table>
<thead>
<tr>
<th>mass, mg</th>
<th>Decalin</th>
<th>Diphenylethane</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>874.687</td>
<td>1.064</td>
<td>11.530</td>
</tr>
</tbody>
</table>

The diluted weight fractions can be calculated using Equations (F.1) for 4-methylstyrene and other hydrogenated products and (F.2) for dimers. From the diluted weight fractions, the actual weight fraction of chemical species $i$ in the product sample can be calculated using Equation (B.1).
Table B.2 GC-MS analysis results.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Area under the peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methylstyrene</td>
<td>631682</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td>251283</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td>60946</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td>72479</td>
</tr>
</tbody>
</table>

\[
C_W^{(i)} = \frac{C_{Wd}^{(i)}}{m_{\text{sample}}} \left( m_{\text{sample}} + m_{\text{decalin}} + m_{\text{DPE}} \right) \quad (B.1)
\]

where,
\[
C_W^{(i)} = \text{actual weight fraction of species } i, \text{ wt}%. \\
C_{Wd}^{(i)} = \text{diluted weight fraction of species } i, \text{ wt}%. \\
m_i = \text{mass, mg.}
\]

The feed conversion, product yields, selectivities can then be calculated as discussed in Section 3.3.5.1. Assuming the density of the product equals the density of the feed (0.878 g/mL) and taking a basis of 100 g of product the concentrations can be calculated using Equation (B.2) as follows:

\[
C_i = \frac{m_i}{M_{W_i} \cdot V} \quad (B.2)
\]
where,

\( m_i \) = mass of chemical species \( i \), mg.

\( C_i \) = concentration of species \( i \), mol/L.

\( MW_i \) = molecular mass of species \( i \), g/mol.

\( V \) = sample volume, mL.

The feed conversion, product yields, selectivities and concentrations are shown in Table B.3.

**Table B.3 Yield, selectivity and conversion results.**

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>( C_{Wd(i)} ), wt%</th>
<th>( C_{W(i)} ), wt%</th>
<th>Yield, wt%</th>
<th>Selectivity, wt%</th>
<th>( C_i ), mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methylstyrene</td>
<td>5.71E-3</td>
<td>4.76</td>
<td>56.0</td>
<td>-</td>
<td>3.53E-1</td>
</tr>
<tr>
<td>1-ethyl-4-methylbenzene</td>
<td>2.64E-3</td>
<td>2.20</td>
<td>25.9</td>
<td>58.9</td>
<td>1.61E-1</td>
</tr>
<tr>
<td>1-ethyl-4-methylcyclohexane</td>
<td>1.11E-3</td>
<td>0.92</td>
<td>10.9</td>
<td>24.7</td>
<td>6.43E-2</td>
</tr>
<tr>
<td>1,3-di-(4'-methylphenyl)butane</td>
<td>7.37E-4</td>
<td>0.61</td>
<td>7.2</td>
<td>16.4</td>
<td>2.26E-2</td>
</tr>
<tr>
<td>Conversion, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>43.3</td>
</tr>
</tbody>
</table>

**B.2 Brunauer, Emmett and Teller (BET) adsorption isotherm [21]**

Brunauer, Emmett and Teller (BET) adsorption isotherm equation is given by Equation (B.3).
\[
\frac{P/P_0}{V(1-P/P_0)} = C - 1\left(\frac{P}{P_0}\right) + \frac{1}{V_mC}
\]  
(B.3)

where,

\[P = \text{equilibrium pressure } i, \text{ mmHg.}\]

\[P_0 = \text{saturation pressure of the adsorbate gas, 760 mmHg.}\]

\[V = \text{volume adsorbed at STP, mL.}\]

\[V_m = \text{volume adsorbed at monolayer coverage at STP, mL.}\]

\[C = \text{constant, dimensionless.}\]

By plotting the left side of the equation versus \(P/P_0\), \(V_m\) can be obtained from the slope and intercept. The BET surface can then be calculated using Equation (B.4).

\[
S_A = \frac{V_m \cdot N_A \cdot a}{m \cdot 22400}
\]

(B.4)

where,

\[S_A = \text{BET surface area, m}^2/\text{g.}\]

\[N_A = \text{Avogadro number, 6.022E23 mol}^{-1}.\]

\[a = \text{effective cross-sectional area of one adsorbate molecule, 1.62E-10 m}^2 \text{ for nitrogen.}\]

\[m = \text{sample mass, g.}\]

22400=adsorbed gas molecular volume (ideal), mL/mol.
B.3 Gum content estimation based on decrease in average reactor bed voidage

Reactor hot zone length = 30 cm

Reactor diameter = 1.18 cm

Reactor volume = 32.808 mL

Table B.4 Gum volume calculation based on decrease in average reactor bed voidage

<table>
<thead>
<tr>
<th>Average reactor bed voidage ($b$)</th>
<th>Void volume mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.39</td>
<td>12.795</td>
</tr>
<tr>
<td>0.12</td>
<td>3.937</td>
</tr>
<tr>
<td>Deposited gum volume, mL</td>
<td>8.858</td>
</tr>
</tbody>
</table>

Assuming gum density = 0.9 g/mL,

Mass of deposited gum = 7.972 g / 30 days

Feed liquid flow = 5 mL/h = 3600 mL / 30 days

Gum content = (7.972 g / 30 days) / (3600 mL / 30 days) = 221 mg / 100 mL
Appendix C  Error analysis

All the reported errors in this thesis are standard errors. The standard error (SE) was calculated using Equation (C.1).

\[
SE = \frac{\sigma}{\sqrt{n}} \tag{C.1}
\]

where,

\[
\sigma = \text{standard deviation} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}
\]

\(n\) = size of the sample.

\(x_i\) = measured value \(i\).

\(\bar{x}\) = average of the measured values = \[
\frac{1}{n} \sum_{i=1}^{n} x_i
\]

C.1  Catalyst characterization

The standard error calculations for the measured BET surface area and CHNS analysis are shown in Tables C.1 and C.2, respectively. Different samples were analyzed from the same catalyst batch.
Table C.1 BET surface area standard error calculations for catalyst recovered from 8.4 wt% 4-methylstyrene hydrogenation for 3 days TOS.

<table>
<thead>
<tr>
<th>$S_A$</th>
<th>$\bar{S}_\lambda$</th>
<th>$\sigma$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m^2/g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>97</td>
<td>5.7</td>
<td>4</td>
</tr>
<tr>
<td>93</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table C.2 Carbon content standard error calculations for the catalyst recovered from 8.4 wt% 4-methylstyrene hydrogenation for 3 days TOS.

<table>
<thead>
<tr>
<th>Carbon content</th>
<th>Average</th>
<th>$\sigma$</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.84</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.56</td>
<td>13.9</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>14.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C.2 GC-MS analysis

The standard error calculations associated with GC-MS analysis are shown in Table C.3.

Table C.3 GC-MS standard error calculations for 4-methylstyrene samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>4-MS area</th>
<th>Average</th>
<th>$\sigma$</th>
<th>SE</th>
<th>SE/Average, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2225491</td>
<td>2131813</td>
<td>108934</td>
<td>62893</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>2157671</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2012277</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3677933</td>
<td>3760899</td>
<td>76153</td>
<td>43967</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>3777147</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3827617</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C.3 Reaction repeatability

As indicated earlier, each set of reaction condition was maintained for at least 3 days TOS and the liquid sample was collected every 24 h. Since the reaction time of 3 days TOS is relatively short, it can be assumed that there was no significant loss of activity during the 3 days of reaction and the standard error can be calculated from the samples collected. The standard error calculations for isoprene hydrogenation are shown in Table C.4 (Feed: 2.4 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr$^{-1}$, H$_2$/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/$\gamma$-Al$_2$O$_3$).
Table C.4 Reaction standard error calculations for 4-methylstyrene samples for isoprene hydrogenation (Feed: 2.4 wt% isoprene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr⁻¹, H₂/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al₂O₃).

<table>
<thead>
<tr>
<th>Yield, wt%</th>
<th>TOS, day</th>
<th>Average</th>
<th>σ</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td>0.1</td>
<td>0.8</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>2-methyl-butane</td>
<td>81.6</td>
<td>81.0</td>
<td>82.4</td>
<td>81.7</td>
</tr>
<tr>
<td>2-methyl-butene</td>
<td>1.2</td>
<td>0.8</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>1-methyl-3-isopropylcyclohexane</td>
<td>11.7%</td>
<td>11.8%</td>
<td>10.6%</td>
<td>11.4%</td>
</tr>
<tr>
<td>1-ethyl-1,3-dimethylcyclohexane</td>
<td>3.7%</td>
<td>4.6%</td>
<td>3.9%</td>
<td>4.1%</td>
</tr>
<tr>
<td>2,6-dimethyloctane + 3,6-dimethyloctane</td>
<td>1.7%</td>
<td>1.1%</td>
<td>1.3%</td>
<td>1.4%</td>
</tr>
<tr>
<td>Conversion</td>
<td>99.94%</td>
<td>99.69%</td>
<td>99.65%</td>
<td>99.76%</td>
</tr>
</tbody>
</table>
Appendix D  Mass transfer, wall effects and axial mass dispersion calculations

The mass transfer coefficient for the diffusion from bulk liquid to external catalyst surface was calculated using Equation (D.1) [79].

\[
k_c = \frac{Sh \cdot D_{AB}}{d_p}
\]  

(D.1)

where

\( k_c \) = mass transfer coefficient for the diffusion from bulk liquid to external catalyst surface, s\(^{-1}\).

\( Sh \) = Sherwood number, dimensionless.

\( D_{AB} \) = diffusivity of A in B, m\(^2\)/s = 1.93E-9 [80].

\( D_{AB0} \) = diffusivity of A in B at standard conditions, m\(^2\)/s = 1.93E-9 [80].

\( d_p \) = pellet diameter (surface area average), m.

Diffusivity of A in B can be calculated using Equation (D.2) [79].

\[
D_{AB} = D_{AB}^{(298\,K)} \cdot \left( \frac{\mu(298\,K)}{\mu} \right) \cdot \left( \frac{T}{298} \right)
\]  

(D.2)

where,

\( D_{AB}^{(298\,K)} \) = diffusivity of A in B, m\(^2\)/s = 1.93E-9 m\(^2\)/s for H\(_2\) in decalin [80].

\( \mu \) = viscosity, kg/(m·s).
\( \mu \) = temperature, K.

Assuming cylindrical pellet, \( d_p \) was calculated using Equation (D.3) [79].

\[
d_p = \sqrt[4]{\frac{A}{\pi}} = \sqrt[4]{\frac{\pi d L_p + 2 \pi (d^2 / 4)}{\pi}}
\]  

(D.3)

where,

\( A = \) external area, m\textsuperscript{2}.

\( d = \) pellet diameter, m.

\( L_p = \) pellet length, m.

The Sherwood number was calculated using Equation (D.4) [79] as follows:

\[
Sh = J_D Re_p Sc^{1/3}
\]  

(D.4)

where,

\( J_D = \) Colburn \( J \) factor.

\( Re_p = \) modified Reynold's number, dimensionless.

\( Sc = \) Schmidt number, dimensionless.

Colburn \( J \) factor was calculated using Equation (D.5) which is valid for liquids in fixed bed reactors with \( Re_p > 0.01 \).
The modified Reynold's number and Schmidt number was calculated using Equations (D.6) and (D.7), respectively [79].

\[
Re_p = \left( \frac{\rho \cdot d_p \cdot U}{\mu} \right) \left( \frac{1}{1 - \varepsilon_p} \right)
\] (D.6)

\[
Sc = \frac{\mu}{\rho \cdot D_{AB}}
\] (D.7)

where

\[ \rho = \text{fluid density, kg/m}^3. \]

\[ U = \text{fluid superficial velocity, m/s.} \]

\[ \varepsilon_{cat} = \text{catalyst bed voidage, dimensionless.} \]

The Mears criterion [81] can be used to determine if external diffusion is limiting. When the Mears criterion is met, external diffusion can be neglected as follows:

\[
\frac{-r_A \cdot d_p \cdot n_r}{2k_c \cdot C_{Ab}} < 0.15
\] (D.8)

where,
\(- r_A = \text{rate of reaction per unit mass of catalyst, mol/(g·h).}\)

\(n_r = \text{reaction order, dimensionless.}\)

\(c_{Av} = \text{bulk concentration of A, mol/L.}\)

Using the feed and catalyst properties listed in Tables D.1 and D.2, the external mass transfer effect was calculated for \(t_1\) day 2 at \(T=250^\circ\text{C}\) which showed the highest apparent reaction rate with \(k_1 = 3.57\times 10^{-3}\) s\(^{-1}\). The results are listed in Table D.3. Since Mear's criterion was met, external diffusion effect was neglected.

**Table D.1 Feed properties at \(T=250^\circ\text{C}\) obtained from Aspen HYSYS V8.8 (Peng Robinson fluid package).**

<table>
<thead>
<tr>
<th>Property</th>
<th>Nomenclature</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>(\rho)</td>
<td>671</td>
<td>kg/m(^3)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>(\mu)</td>
<td>1.41E-4</td>
<td>kg/(m·s)</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>(U)</td>
<td>1.65E-5</td>
<td>m/s</td>
</tr>
</tbody>
</table>
### Table D.2 Properties of catalyst used.

<table>
<thead>
<tr>
<th>Property</th>
<th>Nomenclature</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet diameter</td>
<td>$d$</td>
<td>1.41E-3</td>
<td>m</td>
<td>[77]</td>
</tr>
<tr>
<td>catalyst bed voidage</td>
<td>$\varepsilon_{\text{cat}}$</td>
<td>0.466</td>
<td>dimensionless</td>
<td>[77]</td>
</tr>
<tr>
<td>Pellet length</td>
<td>$L_p$</td>
<td>2.50E-3</td>
<td>m</td>
<td>measured</td>
</tr>
<tr>
<td>Surface area average</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pellet diameter</td>
<td>$d_p$</td>
<td>2.13E-3</td>
<td>m</td>
<td>Equation (D.3)</td>
</tr>
<tr>
<td>Equivalent volume sphere</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pellet diameter</td>
<td>$d_s$</td>
<td>2.02E-3</td>
<td>m</td>
<td>[77]</td>
</tr>
<tr>
<td>Equivalent pellet diameter</td>
<td>$d_e$</td>
<td>1.41E-3</td>
<td>m</td>
<td>[77]</td>
</tr>
</tbody>
</table>

### Table D.3 External mass transfer calculations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>$Re_p$</th>
<th>$Sc$</th>
<th>$J_D$</th>
<th>$Sh$</th>
<th>$D_{AB}$ (250°C)</th>
<th>$k_e$</th>
<th>Mear's criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>m$^2$/s</td>
<td>s$^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>Value</td>
<td>3.13E-1</td>
<td>8.84</td>
<td>5.48</td>
<td>3.55</td>
<td>2.38E-8</td>
<td>3.97E-5</td>
<td>9.56E-2</td>
</tr>
</tbody>
</table>
The internal mass transfer effectiveness factor was calculated using Equation (D.9) as follows:

\[ \eta = \frac{3}{\Phi^2} (\Phi \cdot \coth \Phi - 1) \]  

(D.9)

where

\[ \Phi = \text{Thiele modulus, dimensionless.} \]

The Thiele modulus was calculated using Equation (D.10) [82] as follows:

\[ \Phi = \frac{R}{3} \sqrt{\frac{k}{D_e}} \]  

(D.10)

where

\[ R = \text{pellet radius, m.} \]

\[ k = \text{reaction constant, s}^{-1}. \]

\[ D_e = \text{effective diffusivity, m}^2/\text{s} \approx 0.16 \cdot D_{AB} \]  

[79].

The internal mass transfer can be neglected if the Weisz-Prater's criterion is met as follows [83]:

\[ C_{wp} = \eta \cdot \Phi^2 = 3(\Phi \cdot \coth \Phi - 1) < 0.3 \]  

(D.11)
The internal mass transfer effect was calculated for \( t_1 \) day 2 at \( T=250^\circ C \) which showed the highest apparent reaction rate with \( k_1 = 3.57E-3 \ s^{-1} \). The results are listed in Table D.4. Since Weisz-Prater's criterion was met, internal diffusion effect was neglected.

**Table D.4 Internal mass transfer calculations**

<table>
<thead>
<tr>
<th>Variable</th>
<th>( D_e )</th>
<th>( \Phi )</th>
<th>( \eta )</th>
<th>( C_{WP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>m(^2)/s</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Value</td>
<td>3.80E-9</td>
<td>3.26E-1</td>
<td>0.99</td>
<td>1.05E-1</td>
</tr>
</tbody>
</table>

Therefore, an overall effectiveness factor, \( \Omega = 1 \), was used for all reactions.

To check the significance of axial dispersion and wall effects, the ratio of bed height to equivalent pellet diameter, \( L_n/d_e \), and the ratio of reactor diameter to equivalent pellet diameter, \( d_r/d_e \), were calculated as shown in Table D.5. For comparison, the ratios were also calculated for a commercial reactor. From Table D.5, the \( L_n/d_e \) and \( d_r/d_e \) ratios are much larger for the commercial reactor than the micro-scale reactor used in this study. However, Mears [62] and Doraiswamy and Tajbl [63] indicated that axial mass dispersion and heat conduction can be neglected and plug flow can be closely approximated if \( L_n/d_e \) ratio was larger than 30 for laboratory micro-scale reactors.
As for wall effects, $d_r/d_e$ ratio was found to be larger than 4, satisfying the rule of thumb suggested by Mears [62], Kumar et al. [64] and Doraiswamy and Tajbl [63] for negligible channeling and good liquid distribution at the reactor wall for micro-scale reactors.

Table D.5 Axial dispersion and wall effects calculations for the micro-scale reactor used and a commercial reactor.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bed height</th>
<th>Equivalent pellet diameter</th>
<th>Reactor diameter</th>
<th>Axial dispersion ratio</th>
<th>Wall effects ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nomenclature</td>
<td>$L_o$</td>
<td>$d_e$</td>
<td>$d_r$</td>
<td>$L_o/d_e$</td>
<td>$d_r/d_e$</td>
</tr>
<tr>
<td>Unit</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>dimensionless</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Micro-scale</td>
<td>0.30</td>
<td>1.41E-3</td>
<td>1.18E-2</td>
<td>213</td>
<td>8.37</td>
</tr>
<tr>
<td>Commercial</td>
<td>25</td>
<td>3</td>
<td>17731</td>
<td>2128</td>
<td></td>
</tr>
</tbody>
</table>
Appendix E  Calculation of the minimum amount of the catalyst presulphiding agent

The composition of the catalyst used in this study is shown in Table E.1.

Table E.1 Criterion 424 hydrotreating catalyst composition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>60-85</td>
</tr>
<tr>
<td>MoO₃</td>
<td>15-25</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>NiO</td>
<td>1-6</td>
</tr>
</tbody>
</table>

For 1g of catalyst: \(m_{\text{MoO}_3} = 0.25 \text{ g max}\), and \(m_{\text{NiO}} = 0.06 \text{ g max}\)

\[
\text{MoO}_3 + 2 \text{H}_2\text{S} \xrightarrow{\text{H}_2} \text{MoS}_2 + 3 \text{H}_2\text{O}
\]

\[
3 \text{NiO} + 2 \text{H}_2\text{S} \xrightarrow{\text{H}_2} \text{Ni}_3\text{S}_2 + 3 \text{H}_2\text{O}
\]

\[
N_{\text{MoO}_3} = (0.25 \text{ g})/(143.94 \text{ g/mol}) = 0.0017368 \text{ mol}
\]

\[
N_{\text{NiO}} = (0.06 \text{ g})/(74.6928 \text{ g/mol}) = 0.00080329 \text{ mol}
\]

\[
N (\text{minimum}) = 2 N_{\text{MoO}_3} + 2/3 N_{\text{NiO}} = 0.0040092 \text{ mol}
\]
\[ V_{H_2} \text{ (minimum)} = (3 N_{MoO_3} + N_{NiO} ) \times 24465 \text{ ml/mol} = 147.13 \text{ ml} \]

\[ m_{\text{Butanethiol (minimum)}} = 0.004009 \text{ mol} \times 90.19 \text{ g/mol} \]

\[ m_{\text{Butanethiol (minimum)}} = 0.36157 \text{ g per 1 g of catalyst} \]

\[ V_{\text{Butanethiol (minimum)}} = (0.36157 \text{ g})/(0.83679 \text{ g/cm}^3) \]

\[ V_{\text{Butanethiol (minimum)}} = 0.43211 \text{ cm}^3 \text{ per 1 g of catalyst} \]
Appendix F  Gas chromatography-mass spectrometry (GC-MS)

In this appendix, GC-MS sample preparation method, parameters and calibrations used in this study are discussed.

F.1  Sample preparation

In order to avoid column overloading/detector saturation, the feed or product sample needs to be diluted in decalin. The GC-MS sample was prepared as follows:

- Add ~2 mg of 1,1-diphenylethylene (DPE) to a 2 mL Supleco clear glass vial.
- Using Gilson Pipetman P1000G variable volume pipette, 1000 μL of decalin was pipetted to a 2 mL Supleco clear glass vial.
- The weight of decalin was then measured and recorded to the nearest 0.001 mg.
- Using Gilson Pipetman P20G variable volume pipette, 15-20 μL of feed or product sample was pipetted to the 2 mL Supleco clear glass vial containing the decalin.
- The sample was then sealed with PTFE/silicone/PTFE septum crimp seal
- The weight of the feed or product sample was then measured and recorded to the nearest 0.001 mg.

F.2  GC-MS parameters

The sampler, GC and MS parameters in Shimadzu GC-MS-QP2010 are shown in Figures F.1, F.2 and F.3, respectively.
Figure F.1 Auto-sampler parameters in Shimadzu GC-MS-QP2010.

Figure F.2 GC parameters in Shimadzu GC-MS-QP2010.
Figure F.3 MS parameters in Shimadzu GC-MS-QP2010.

F.3 GC-MS calibration

The calibration data for 4-methylstyrene and 1,1-diphenylhexane are shown in Tables F.1 and F.2, respectively. By a linear fit of 4-methylstyrene and C18 weight concentrations versus corresponding GC-MS areas as shown in Figures F.4 and F.5, resulted in Equations (F.1) and (F.2) as follows, respectively:

\[
C_{Wd(4-MS)} = 8.73 \times 10^{-8} \cdot A_{GC-MS(4-MS)} + 6.69 \times 10^{-3} \quad \text{(F.1)}
\]

\[
C_{Wd(C18)} = 7.35 \times 10^{-8} \cdot A_{GC-MS(C18)} + 2.66 \times 10^{-3} \quad \text{(F.2)}
\]

where,

\( A_{GC-MS} = \) GC-MS area under the peak.

\( C_{Wd(i)} = \) diluted weight fraction of species \( i \), wt%.
Table F.1 Calibration data for 4-methylstyrene (4-MS) in Shimadzu GC-MS-QP2010.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Initial sample prep</th>
<th>Sample dilution</th>
<th>GCMS Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4-MS</td>
<td>Decalin</td>
<td>4-MS concentration</td>
</tr>
<tr>
<td></td>
<td>(mg)</td>
<td>(mg)</td>
<td>(w%)</td>
</tr>
<tr>
<td>1</td>
<td>4.776</td>
<td>877.940</td>
<td>0.541</td>
</tr>
<tr>
<td>2</td>
<td>4.776</td>
<td>877.940</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>8.921</td>
<td>879.340</td>
<td>1.004</td>
</tr>
<tr>
<td>4</td>
<td>8.921</td>
<td>879.340</td>
<td>1.004</td>
</tr>
<tr>
<td>5</td>
<td>8.921</td>
<td>879.340</td>
<td>1.004</td>
</tr>
<tr>
<td>6</td>
<td>17.834</td>
<td>878.227</td>
<td>1.990</td>
</tr>
<tr>
<td>7</td>
<td>17.834</td>
<td>878.227</td>
<td>1.990</td>
</tr>
<tr>
<td>8</td>
<td>17.834</td>
<td>878.227</td>
<td>1.990</td>
</tr>
<tr>
<td>9</td>
<td>47.655</td>
<td>882.392</td>
<td>5.124</td>
</tr>
<tr>
<td>10</td>
<td>47.655</td>
<td>882.392</td>
<td>5.124</td>
</tr>
<tr>
<td>11</td>
<td>47.655</td>
<td>882.392</td>
<td>5.124</td>
</tr>
<tr>
<td>12</td>
<td>88.082</td>
<td>885.620</td>
<td>9.046</td>
</tr>
<tr>
<td>13</td>
<td>88.082</td>
<td>885.620</td>
<td>9.046</td>
</tr>
<tr>
<td>14</td>
<td>88.082</td>
<td>885.620</td>
<td>9.046</td>
</tr>
</tbody>
</table>
Table F.2 Calibration data for 1,1-diphenylhexane (DPH) in Shimadzu GC-MS-QP2010.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Initial sample prep</th>
<th>Sample dilution</th>
<th>GCMS Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPH (mg)</td>
<td>Decalin (mg)</td>
<td>DPH concentration (wt%)</td>
</tr>
<tr>
<td>1</td>
<td>5.05</td>
<td>886.922</td>
<td>0.566</td>
</tr>
<tr>
<td>2</td>
<td>5.05</td>
<td>886.922</td>
<td>0.566</td>
</tr>
<tr>
<td>3</td>
<td>5.05</td>
<td>886.922</td>
<td>0.566</td>
</tr>
<tr>
<td>4</td>
<td>10.094</td>
<td>884.697</td>
<td>1.128</td>
</tr>
<tr>
<td>5</td>
<td>10.094</td>
<td>884.697</td>
<td>1.128</td>
</tr>
<tr>
<td>6</td>
<td>10.094</td>
<td>884.697</td>
<td>1.128</td>
</tr>
<tr>
<td>7</td>
<td>19.08</td>
<td>880.740</td>
<td>2.120</td>
</tr>
<tr>
<td>8</td>
<td>19.08</td>
<td>880.740</td>
<td>2.120</td>
</tr>
<tr>
<td>9</td>
<td>19.08</td>
<td>880.740</td>
<td>2.120</td>
</tr>
<tr>
<td>10</td>
<td>47.527</td>
<td>886.544</td>
<td>5.088</td>
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<tr>
<td>11</td>
<td>47.527</td>
<td>886.544</td>
<td>5.088</td>
</tr>
<tr>
<td>12</td>
<td>47.527</td>
<td>886.544</td>
<td>5.088</td>
</tr>
<tr>
<td>13</td>
<td>83.975</td>
<td>881.570</td>
<td>8.697</td>
</tr>
<tr>
<td>14</td>
<td>83.975</td>
<td>881.570</td>
<td>8.697</td>
</tr>
<tr>
<td>15</td>
<td>83.975</td>
<td>881.570</td>
<td>8.697</td>
</tr>
</tbody>
</table>
Figure F.4 Calibration curve for 4-methylstyrene (4-MS) in Shimadzu GC-MS-QP2010.

Figure F.5 Calibration curve for 1,1-diphenylhexane (DPH) in Shimadzu GC-MS-QP2010.
Appendix G  $^{13}$C NMR results

In this appendix, higher resolution $^{13}$C NMR figures are included. Figures G.1 to G.5 show the analysis results for 4-methylstyrene reaction product after 30 days TOS (Feed: 8.4% 4-methylstyrene in decalin, T=250°C, P=3.4 MPa, LHSV=2 hr$^{-1}$, H$_2$/feed=392 standard mL/mL, catalyst: spent Ni-Mo-S/γ-Al$_2$O$_3$). Figures G.6 to G.9 show the analysis results for the gum recovered from the same sample.
Figure G.1 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS (145-124 ppm).
Figure G.2 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS (47-15ppm).
Figure G.3 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS (47-33ppm).
Figure G.4 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS (30-16 ppm).
Figure G.5 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product after 30 days TOS (30-16 ppm-higher resolution).
Figure G.6 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product gum after 30 days TOS (148-132 ppm).
Figure G.7 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product gum after 30 days TOS (131-125 ppm).
Figure G.8 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product gum after 30 days TOS (49-39 ppm).
Figure G.9 $^{13}$C-NMR spectrum for 8.4 wt% 4-methylstyrene in decalin reaction product gum after 30 days TOS (39-19 ppm).
Appendix H  Kinetic model MATLAB code

H.1  Main body code

clear all

% catalyst mass (g)
M=[0 0.5 1 2];
M_250=[0 0.5 1];

% Concentrations (mol/L)
%              4MS          HYD         C18         cC6=       cC6
T150_day2=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          4.27280E-01 1.61112E-01 1.77358E-02 1.98034E+00 1.56939E-01
          1.21761E-01 5.02108E-01 0.00000E+00 1.90695E+00 2.30020E-01
          7.11589E-02 5.13500E-01 1.96047E-02 9.67867E-01 1.16910E+00];
T150_day3=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          4.43856E-01 1.33414E-01 7.70931E-02 2.01076E+00 1.26204E-01
          1.65771E-01 4.32998E-01 1.25495E-02 1.78428E+00 1.78428E-01
          1.01606E-01 4.69726E-01 2.62681E-02 1.14548E+00 9.91484E-01];
T180_day2=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          1.93943E-01 2.88458E-01 7.07335E-02 1.65920E+00 4.77770E-01
          8.96240E-02 4.91791E-01 2.12243E-02 8.82878E-01 8.82878E-01
          0.00000E+00 5.81481E-01 2.11914E-02 3.88921E-01 1.74805E+00];
T180_day3=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          2.40476E-01 2.41483E-01 7.09358E-02 1.79082E+00 3.46145E-01
          1.30490E-01 4.44122E-01 2.46255E-02 1.47425E+00 6.62718E-01
          3.43447E-02 5.15937E-01 3.67908E-02 6.17749E-01 1.51922E+00];
T200_day2=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          1.68024E-01 3.83204E-01 3.63180E-02 1.58258E+00 5.54391E-01
          6.28642E-02 5.13368E-01 2.38155E-02 1.11288E+00 1.02409E+00
          5.34448E-02 4.27324E-01 7.15475E-02 8.17420E-01 1.31955E+00];
T200_day3=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          2.38809E-01 3.13548E-01 3.57352E-02 1.72453E+00 4.12440E-01
          1.15851E-01 4.67347E-01 2.03328E-02 1.33605E+00 8.00913E-01
          6.94669E-02 3.96351E-01 7.90227E-02 1.05341E+00 1.08355E+00];
T250_day2=[6.23863E-01 0.00000E+00 0.00000E+00 2.13697E+00 0.00000E+00
          5.48175E-02 5.30272E-01 1.93869E-02 1.9473E+00 9.42236E-01
          3.8993E-02 5.50914E-01 1.95251E-02 3.94127E-01 1.74284E+00];
C_4MS_X_T150_day2=T150_day2(:,1);  
C_HYD_X_T150_day2=T150_day2(:,2);  
C_C18_X_T150_day2=T150_day2(:,3);  
C_cC6ene_X_T150_day2=T150_day2(:,4);  
C_cC6_X_T150_day2=T150_day2(:,5);  
C_4MS_X_T180_day2=T180_day2(:,1);  
C_HYD_X_T180_day2=T180_day2(:,2);  
C_C18_X_T180_day2=T180_day2(:,3);  
C_cC6ene_X_T180_day2=T180_day2(:,4);  
C_cC6_X_T180_day2=T180_day2(:,5);  
C_4MS_X_T200_day2=T200_day2(:,1);  
C_HYD_X_T200_day2=T200_day2(:,2);  
C_C18_X_T200_day2=T200_day2(:,3);  
C_cC6ene_X_T200_day2=T200_day2(:,4);  
C_cC6_X_T200_day2=T200_day2(:,5);  
C_4MS_X_T250_day2=T250_day2(:,1);  
C_HYD_X_T250_day2=T250_day2(:,2);  
C_C18_X_T250_day2=T250_day2(:,3);  
C_cC6ene_X_T250_day2=T250_day2(:,4);  
C_cC6_X_T250_day2=T250_day2(:,5);  
C_4MS_X_T150_day3=T150_day3(:,1);  
C_HYD_X_T150_day3=T150_day3(:,2);  
C_C18_X_T150_day3=T150_day3(:,3);  
C_cC6ene_X_T150_day3=T150_day3(:,4);  
C_cC6_X_T150_day3=T150_day3(:,5);  
C_4MS_X_T180_day3=T180_day3(:,1);  
C_HYD_X_T180_day3=T180_day3(:,2);  
C_C18_X_T180_day3=T180_day3(:,3);  
C_cC6ene_X_T180_day3=T180_day3(:,4);  
C_cC6_X_T180_day3=T180_day3(:,5);  
C_4MS_X_T200_day3=T200_day3(:,1);  
C_HYD_X_T200_day3=T200_day3(:,2);  
C_C18_X_T200_day3=T200_day3(:,3);  
C_cC6ene_X_T200_day3=T200_day3(:,4);  
C_cC6_X_T200_day3=T200_day3(:,5);  
C_4MS_X_T250_day3=T250_day3(:,1);  
C_HYD_X_T250_day3=T250_day3(:,2);  
C_C18_X_T250_day3=T250_day3(:,3);  
C_cC6ene_X_T250_day3=T250_day3(:,4);  
C_cC6_X_T250_day3=T250_day3(:,5);
\[ T_{150} = 150 + 273.15; \]
\[ T_{180} = 180 + 273.15; \]
\[ T_{200} = 200 + 273.15; \]
\[ T_{250} = 250 + 273.15; \]

\[ T_{\text{ref}} = \text{mean}(T_{150} + T_{180} + T_{200} + T_{250}); \]

options = optimset('display', 'iter', 'LargeScale', 'off', 'MaxIter', 10000, ...
'MaxFunEvals', 30000, ' TolX', 1e-10, ' TolFUN', 1e-10);

lb = [0 0]; % lower bound for parameters
ub = [inf inf]; % Upper bound for parameters

lbC6 = 0; % lower bound for parameters (C6)
ubC6 = inf; % Upper bound for parameters (C6)

v0 = 5; % feed volumetric flow rate in mL/h at std conditions

\[
\text{v0T} = [5.66844225 \\
5.87767489 \\
6.032909292 \\
6.506113928];
\]

bed_porosity = 0.466; % for trilobe shaped catalyst
den_bed = 0.8*(1 - bed_porosity); % g/mL

% initial guess for parameters

% initial estimates for \( k1/v_0 \) (1/g) \( k2/v_0 \) (L/(mol.g))
p0_150 = [10 3];
p0_180 = [0.1 0.01];
p0_200 = [5 0.4];
p0_250 = [10 5];

% initial estimates for \( k3/v_0 \) (1/g)
p0C6_150 = 0.76/v0/den_bed;
p0C6_180 = 2.5/v0/den_bed;
p0C6_200 = 3/v0/den_bed;
p0C6_250 = 5/v0/den_bed;

% Set initial concentrations
C_4MS_0 = C_4MS_X_T150_day2(1);
C_HYD_0 = C_HYD_X_T150_day2(1);
C_C18_0 = C_C18_X_T150_day2(1);
C_cC6ene_0 = C_cC6ene_X_T150_day2(1);
C_cC6_0 = C_cC6_X_T150_day2(1);

C_0_4MS = [C_4MS_0; C_HYD_0; C_C18_0];
C_0_C6 = [C_cC6ene_0; C_cC6_0];
\[ p_{150\ _day3}, S_{150\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{150}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{4MS\ X\ T150\ _day3}, \text{C}_{HYD\ X\ T150\ _day3}, \]
\[ C_{C18\ X\ T150\ _day3}; \]
\[ p_{180\ _day3}, S_{180\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{180}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{4MS\ X\ T180\ _day3}, \text{C}_{HYD\ X\ T180\ _day3}, \]
\[ C_{C18\ X\ T180\ _day3}; \]
\[ p_{200\ _day3}, S_{200\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{200}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{4MS\ X\ T200\ _day3}, \text{C}_{HYD\ X\ T200\ _day3}, \]
\[ C_{C18\ X\ T200\ _day3}; \]
\[ p_{250\ _day3}, S_{250\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{250}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{250}, \text{C}_{4MS\ X\ T250\ _day3}, \text{C}_{HYD\ X\ T250\ _day3}, \]
\[ C_{C18\ X\ T250\ _day3}; \]
\[ p_{150\ _day2}, S_{150\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{150}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T150\ _day2}, \text{C}_{cC6\ X\ T150\ _day2}; \]
\[ p_{180\ _day2}, S_{180\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{180}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{4MS\ X\ T180\ _day2}, \text{C}_{HYD\ X\ T180\ _day2}, \]
\[ C_{cC6\ X\ T180\ _day2}; \]
\[ p_{200\ _day2}, S_{200\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{200}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{4MS\ X\ T200\ _day2}, \text{C}_{HYD\ X\ T200\ _day2}, \]
\[ C_{cC6\ X\ T200\ _day2}; \]
\[ p_{250\ _day2}, S_{250\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_Thesis\_all\_noC18}, \]
\[ p_0_{250}, \text{lb}, \text{ub}, \text{options}, \text{M}, \text{C}_{250}, \text{C}_{4MS\ X\ T250\ _day2}, \text{C}_{HYD\ X\ T250\ _day2}, \]
\[ C_{cC6\ X\ T250\ _day2}; \]
\[ p_{c6\ _150\ _day3}, S_{c6\ _150\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _150}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T150\ _day3}, \]
\[ C_{cC6\ X\ T150\ _day3}; \]
\[ p_{c6\ _180\ _day3}, S_{c6\ _180\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _180}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T180\ _day3}, \]
\[ C_{cC6\ X\ T180\ _day3}; \]
\[ p_{c6\ _200\ _day3}, S_{c6\ _200\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _200}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T200\ _day3}, \]
\[ C_{cC6\ X\ T200\ _day3}; \]
\[ p_{c6\ _250\ _day3}, S_{c6\ _250\ _day3} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _250}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T250\ _day3}, \]
\[ C_{cC6\ X\ T250\ _day3}; \]
\[ p_{c6\ _150\ _day2}, S_{c6\ _150\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _150}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T150\ _day2}, \]
\[ C_{cC6\ X\ T150\ _day2}; \]
\[ p_{c6\ _180\ _day2}, S_{c6\ _180\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _180}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T180\ _day2}, \]
\[ C_{cC6\ X\ T180\ _day2}; \]
\[ p_{c6\ _200\ _day2}, S_{c6\ _200\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _200}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T200\ _day2}, \]
\[ C_{cC6\ X\ T200\ _day2}; \]
\[ p_{c6\ _250\ _day2}, S_{c6\ _250\ _day2} = \text{fminsearchbnd}(@\text{OBJECTIVE\_FUN\_MLE\_ThesisC6\ all}, \]
\[ p_{0c6\ _250}, \text{lbC6}, \text{ubC6}, \text{options}, \text{M}, \text{C}_{cC6ene\ X\ T250\ _day2}, \]
\[ C_{cC6\ X\ T250\ _day2}; \]
p0C6_180,lbC6,ubC6, options,M_cC6ene_X_T180_day2,C_cC6_X_T180_day2);

[pC6_200_day2,SC6_200_day2]=fminsearchbnd(@OBJECTIVE_FUN_MLE_ThesisC6_all,...
    p0C6_200,lbC6,ubC6, options,M_cC6ene_X_T200_day2,C_cC6_X_T200_day2);

[pC6_250_day2,SC6_250_day2]=fminsearchbnd(@OBJECTIVE_FUN_MLE_ThesisC6_all,...
    p0C6_250,lbC6,ubC6, options,M_250,C_cC6ene_X_T250_day2,...
    C_cC6_X_T250_day2);

v0T=[5.66844225
     5.877677489
     6.032909292
     6.506113928];

% extracting k1 (1/h), k2(L/(mol.h) and k3 (1/h)

k1_150_day3=p_150_day3(1)*v0T(1)*den_bed;
k2_150_day3=p_150_day3(2)*v0T(1)*den_bed;
kC6_150_day3=pC6_150_day3*v0T(1)*den_bed;

k1_180_day3=p_180_day3(1)*v0T(2)*den_bed;
k2_180_day3=p_180_day3(2)*v0T(2)*den_bed;
kC6_180_day3=pC6_180_day3*v0T(2)*den_bed;

k1_200_day3=p_200_day3(1)*v0T(3)*den_bed;
k2_200_day3=p_200_day3(2)*v0T(3)*den_bed;
kC6_200_day3=pC6_200_day3*v0T(3)*den_bed;

k1_250_day3=p_250_day3(1)*v0T(4)*den_bed;
k2_250_day3=p_250_day3(2)*v0T(4)*den_bed;
kC6_250_day3=pC6_250_day3*v0T(4)*den_bed;

k1_150_day2=p_150_day2(1)*v0T(1)*den_bed;
k2_150_day2=p_150_day2(2)*v0T(1)*den_bed;
kC6_150_day2=pC6_150_day2*v0T(1)*den_bed;

k1_180_day2=p_180_day2(1)*v0T(2)*den_bed;
k2_180_day2=p_180_day2(2)*v0T(2)*den_bed;
kC6_180_day2=pC6_180_day2*v0T(2)*den_bed;

k1_200_day2=p_200_day2(1)*v0T(3)*den_bed;
k2_200_day2=p_200_day2(2)*v0T(3)*den_bed;
kC6_200_day2=pC6_200_day2*v0T(3)*den_bed;

k1_250_day2=p_250_day2(1)*v0T(4)*den_bed;
k2_250_day2=p_250_day2(2)*v0T(4)*den_bed;
kC6_250_day2=pC6_250_day2*v0T(4)*den_bed;

% Model values calculation

mspan=0:.01:2;
[m,Y_150_day3] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_150_day3);
[m,Y_180_day3] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_180_day3);
[m,Y_200_day3] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_200_day3);
[m,Y_250_day3] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_250_day3);

[m,Y_150_day2] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_150_day2);
[m,Y_180_day2] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_180_day2);
[m,Y_200_day2] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_200_day2);
[m,Y_250_day2] = ode45('ODE_FUN_Thesis',mspan,C_0_4MS,[],p_250_day2);

[m,YC6ene_150_day3] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_150_day3);
[m,YC6ene_180_day3] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_180_day3);
[m,YC6ene_200_day3] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_200_day3);
[m,YC6ene_250_day3] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_250_day3);

[m,YC6ene_150_day2] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_150_day2);
[m,YC6ene_180_day2] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_180_day2);
[m,YC6ene_200_day2] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_200_day2);
[m,YC6ene_250_day2] = ode45('ODE_FUN_ThesisC6',mspan,C_0_C6,[],pC6_250_day2);

% Extracting calculated model concentrations

C_4MS_T150_day3 = real(abs(Y_150_day3(:,1)));  
C_HYD_T150_day3 = real(abs(Y_150_day3(:,2)));  
C_C18_T150_day3 = real(abs(Y_150_day3(:,3)));  
C_cC6ene_T150_day3 = real(abs(YC6ene_150_day3(:,1)));  
C_4MS_T180_day3 = real(abs(Y_180_day3(:,1)));  
C_HYD_T180_day3 = real(abs(Y_180_day3(:,2)));  
C_C18_T180_day3 = real(abs(Y_180_day3(:,3)));  
C_cC6ene_T180_day3 = real(abs(YC6ene_180_day3(:,1)));  
C_4MS_T200_day3 = real(abs(Y_200_day3(:,1)));  
C_HYD_T200_day3 = real(abs(Y_200_day3(:,2)));  
C_C18_T200_day3 = real(abs(Y_200_day3(:,3)));  
C_cC6ene_T200_day3 = real(abs(YC6ene_200_day3(:,1)));  
C_4MS_T250_day3 = real(abs(Y_250_day3(:,1)));  
C_HYD_T250_day3 = real(abs(Y_250_day3(:,2)));  
C_C18_T250_day3 = real(abs(Y_250_day3(:,3)));  
C_cC6ene_T250_day3 = real(abs(YC6ene_250_day3(:,1)));  
C_4MS_T150_day2 = real(abs(Y_150_day2(:,1)));  
C_HYD_T150_day2 = real(abs(Y_150_day2(:,2)));  
C_C18_T150_day2 = real(abs(Y_150_day2(:,3)));  
C_cC6ene_T150_day2 = real(abs(YC6ene_150_day2(:,1)));  
C_4MS_T180_day2 = real(abs(Y_180_day2(:,1)));  
C_HYD_T180_day2 = real(abs(Y_180_day2(:,2)));  
C_C18_T180_day2 = real(abs(Y_180_day2(:,3)));  
C_cC6ene_T180_day2 = real(abs(YC6ene_180_day2(:,1)));
C_4MS_T200_day2  =real(abs(Y_200_day2(:,1)));  
C_HYD_T200_day2  =real(abs(Y_200_day2(:,2)));  
C_C18_T200_day2  =real(abs(Y_200_day2(:,3)));  
C_cC6ene_T200_day2  =real(abs(YC6ene_200_day2(:,1)));  

C_4MS_T250_day2  =real(abs(Y_250_day2(:,1)));  
C_HYD_T250_day2  =real(abs(Y_250_day2(:,2)));  
C_C18_T250_day2  =real(abs(Y_250_day2(:,3)));  
C_cC6ene_T250_day2  =real(abs(YC6ene_250_day2(:,1)));  

C_cC6_T150_day3  =real(abs(YC6ene_150_day3(:,2)));  
C_cC6_T180_day3  =real(abs(YC6ene_180_day3(:,2)));  
C_cC6_T200_day3  =real(abs(YC6ene_200_day3(:,2)));  
C_cC6_T250_day3  =real(abs(YC6ene_250_day3(:,2)));  

C_cC6_T150_day2  =real(abs(YC6ene_150_day2(:,2)));  
C_cC6_T180_day2  =real(abs(YC6ene_180_day2(:,2)));  
C_cC6_T200_day2  =real(abs(YC6ene_200_day2(:,2)));  
C_cC6_T250_day2  =real(abs(YC6ene_250_day2(:,2)));  

% Model degree of explanation calculations  
C_4MS_T150_day2E  =real(abs([C_4MS_T150_day2(1) C_4MS_T150_day2(51) ... 
                           C_4MS_T150_day2(101) C_4MS_T150_day2(201)]));  
C_HYD_T150_day2E  =real(abs([C_HYD_T150_day2(1) C_HYD_T150_day2(51) ... 
                           C_HYD_T150_day2(101) C_HYD_T150_day2(201)]));  
C_C18_T150_day2E  =real(abs([C_C18_T150_day2(1) C_C18_T150_day2(51) ... 
                           C_C18_T150_day2(101) C_C18_T150_day2(201)]));  

C_4MS_T180_day2E  =real(abs([C_4MS_T180_day2(1) C_4MS_T180_day2(51) ... 
                           C_4MS_T180_day2(101) C_4MS_T180_day2(201)]));  
C_HYD_T180_day2E  =real(abs([C_HYD_T180_day2(1) C_HYD_T180_day2(51) ... 
                           C_HYD_T180_day2(101) C_HYD_T180_day2(201)]));  
C_C18_T180_day2E  =real(abs([C_C18_T180_day2(1) C_C18_T180_day2(51) ... 
                           C_C18_T180_day2(101) C_C18_T180_day2(201)]));  

C_4MS_T200_day2E  =real(abs([C_4MS_T200_day2(1) C_4MS_T200_day2(51) ... 
                           C_4MS_T200_day2(101) C_4MS_T200_day2(201)]));  
C_HYD_T200_day2E  =real(abs([C_HYD_T200_day2(1) C_HYD_T200_day2(51) ... 
                           C_HYD_T200_day2(101) C_HYD_T200_day2(201)]));  
C_C18_T200_day2E  =real(abs([C_C18_T200_day2(1) C_C18_T200_day2(51) ... 
                           C_C18_T200_day2(101) C_C18_T200_day2(201)]));  

C_4MS_T250_day2E  =real(abs([C_4MS_T250_day2(1) C_4MS_T250_day2(51) ... 
                           C_4MS_T250_day2(101) C_4MS_T250_day2(201)]));  
C_HYD_T250_day2E  =real(abs([C_HYD_T250_day2(1) C_HYD_T250_day2(51) ... 
                           C_HYD_T250_day2(101) C_HYD_T250_day2(201)]));  
C_C18_T250_day2E  =real(abs([C_C18_T250_day2(1) C_C18_T250_day2(51) ... 
                           C_C18_T250_day2(101) C_C18_T250_day2(201)]));  

C_4MS_T150_day3E  =real(abs([C_4MS_T150_day3(1) C_4MS_T150_day3(51) ... 
                           C_4MS_T150_day3(101) C_4MS_T150_day3(201)]));
C_HYD_T150_day3E = real(abs([C_HYD_T150_day3(1) C_HYD_T150_day3(51) ...
C_HYD_T150_day3(101) C_HYD_T150_day3(201)]));
C_C18_T150_day3E = real(abs([C_C18_T150_day3(1) C_C18_T150_day3(51) ...
C_C18_T150_day3(101) C_C18_T150_day3(201)]));
C_4MS_T180_day3E = real(abs([C_4MS_T180_day3(1) C_4MS_T180_day3(51) ...
C_4MS_T180_day3(101) C_4MS_T180_day3(201)]));
C_HYD_T180_day3E = real(abs([C_HYD_T180_day3(1) C_HYD_T180_day3(51) ...
C_HYD_T180_day3(101) C_HYD_T180_day3(201)]));
C_C18_T180_day3E = real(abs([C_C18_T180_day3(1) C_C18_T180_day3(51) ...
C_C18_T180_day3(101) C_C18_T180_day3(201)]));
C_4MS_T200_day3E = real(abs([C_4MS_T200_day3(1) C_4MS_T200_day3(51) ...
C_4MS_T200_day3(101) C_4MS_T200_day3(201)]));
C_HYD_T200_day3E = real(abs([C_HYD_T200_day3(1) C_HYD_T200_day3(51) ...
C_HYD_T200_day3(101) C_HYD_T200_day3(201)]));
C_C18_T200_day3E = real(abs([C_C18_T200_day3(1) C_C18_T200_day3(51) ...
C_C18_T200_day3(101) C_C18_T200_day3(201)]));
C_4MS_T250_day3E = real(abs([C_4MS_T250_day3(1) C_4MS_T250_day3(51) ...
C_4MS_T250_day3(101)]));
C_HYD_T250_day3E = real(abs([C_HYD_T250_day3(1) C_HYD_T250_day3(51) ...
C_HYD_T250_day3(101)]));
C_C18_T250_day3E = real(abs([C_C18_T250_day3(1) C_C18_T250_day3(51) ...
C_C18_T250_day3(101)]));
C_cC6ene_T150_day2E = real(abs([C_cC6ene_T150_day2(1) ...
C_cC6ene_T150_day2(51) C_cC6ene_T150_day2(101) ...
C_cC6ene_T150_day2(201)]));
C_cC6ene_T180_day2E = real(abs([C_cC6ene_T180_day2(1) ...
C_cC6ene_T180_day2(51) C_cC6ene_T180_day2(101) ...
C_cC6ene_T180_day2(201)]));
C_cC6ene_T200_day2E = real(abs([C_cC6ene_T200_day2(1) ...
C_cC6ene_T200_day2(51) C_cC6ene_T200_day2(101) ...
C_cC6ene_T200_day2(201)]));
C_cC6ene_T250_day2E = real(abs([C_cC6ene_T250_day2(1) ...
C_cC6ene_T250_day2(51) C_cC6ene_T250_day2(101)]));
C_cC6ene_T150_day3E = real(abs([C_cC6ene_T150_day3(1) ...
C_cC6ene_T150_day3(51) C_cC6ene_T150_day3(101) ...
C_cC6ene_T150_day3(201)]));
C_cC6ene_T180_day3E = real(abs([C_cC6ene_T180_day3(1) ...
C_cC6ene_T180_day3(51) C_cC6ene_T180_day3(101) ...
C_cC6ene_T180_day3(201)]));
C_cC6ene_T200_day3E = real(abs([C_cC6ene_T200_day3(1) ...
C_cC6ene_T200_day3(51) C_cC6ene_T200_day3(101) ...
C_cC6ene_T200_day3(201)]));
C_cC6ene_T250_day3E = real(abs([C_cC6ene_T250_day3(1) ...
C_cC6ene_T250_day3(51) C_cC6ene_T250_day3(101)]));
R2_4MS_T150_day2 = 1-sum((C_4MS_X_T150_day2-C_4MS_T150_day2E).^2)/... sum((C_4MS_X_T150_day2-mean(C_4MS_X_T150_day2)).^2);
R2_HYD_T150_day2 = 1-sum((C_HYD_X_T150_day2-C_HYD_T150_day2E).^2)/...
sum((C_HYD_X_T150_day2-mean(C_HYD_X_T150_day2)).^2);
R2_C18_T150_day2=1-sum((C_C18_X_T150_day2-C_C18_T150_day2E).^2)/
sum((C_C18_X_T150_day2-mean(C_C18_X_T150_day2)).^2);
R2_T150_day2=1-sum((C_4MS_X_T150_day2-C_4MS_T150_day2E).^2+
(C_HYD_X_T150_day2-C_HYD_T150_day2E).^2+
(C_C18_X_T150_day2-mean(C_C18_X_T150_day2)).^2);
Residual_4MS_T150_day2=C_4MS_X_T150_day2-C_4MS_T150_day2E;
Residual_HYD_T150_day2=C_HYD_X_T150_day2-C_HYD_T150_day2E;
Residual_C18_T150_day2=C_C18_X_T150_day2-C_C18_T150_day2E;

R2_4MS_T150_day3=1-sum((C_4MS_X_T150_day3-C_4MS_T150_day3E).^2)/
sum((C_4MS_X_T150_day3-mean(C_4MS_X_T150_day3)).^2);
R2_HYD_T150_day3=1-sum((C_HYD_X_T150_day3-C_HYD_T150_day3E).^2)/
sum((C_HYD_X_T150_day3-mean(C_HYD_X_T150_day3)).^2);
R2_C18_T150_day3=1-sum((C_C18_X_T150_day3-C_C18_T150_day3E).^2)/
sum((C_C18_X_T150_day3-mean(C_C18_X_T150_day3)).^2);

R2_T150_day3=1-sum((C_4MS_X_T150_day3-C_4MS_T150_day3E).^2+
(C_HYD_X_T150_day3-C_HYD_T150_day3E).^2+
(C_C18_X_T150_day3-mean(C_C18_X_T150_day3)).^2);

Residual_4MS_T150_day3=C_4MS_X_T150_day3-C_4MS_T150_day3E;
Residual_HYD_T150_day3=C_HYD_X_T150_day3-C_HYD_T150_day3E;
Residual_C18_T150_day3=C_C18_X_T150_day3-C_C18_T150_day3E;

R2_4MS_T180_day2=1-sum((C_4MS_X_T180_day2-C_4MS_T180_day2E).^2)/
sum((C_4MS_X_T180_day2-mean(C_4MS_X_T180_day2)).^2);
R2_HYD_T180_day2=1-sum((C_HYD_X_T180_day2-C_HYD_T180_day2E).^2)/
sum((C_HYD_X_T180_day2-mean(C_HYD_X_T180_day2)).^2);
R2_C18_T180_day2=1-sum((C_C18_X_T180_day2-C_C18_T180_day2E).^2)/
sum((C_C18_X_T180_day2-mean(C_C18_X_T180_day2)).^2);

R2_T180_day2=1-sum((C_4MS_X_T180_day2-C_4MS_T180_day2E).^2+
(C_HYD_X_T180_day2-C_HYD_T180_day2E).^2+
(C_C18_X_T180_day2-mean(C_C18_X_T180_day2)).^2);

Residual_4MS_T180_day2=C_4MS_X_T180_day2-C_4MS_T180_day2E;
Residual_HYD_T180_day2=C_HYD_X_T180_day2-C_HYD_T180_day2E;
Residual_C18_T180_day2=C_C18_X_T180_day2-C_C18_T180_day2E;

R2_4MS_T180_day3=1-sum((C_4MS_X_T180_day3-C_4MS_T180_day3E).^2)/
sum((C_4MS_X_T180_day3-mean(C_4MS_X_T180_day3)).^2);
R2_HYD_T180_day3=1-sum((C_HYD_X_T180_day3-C_HYD_T180_day3E).^2)/
sum((C_HYD_X_T180_day3-mean(C_HYD_X_T180_day3)).^2);
R2_C18_T180_day3=1-sum((C_C18_X_T180_day3-C_C18_T180_day3E).^2)/
sum((C_C18_X_T180_day3-mean(C_C18_X_T180_day3)).^2);

R2_T180_day3=1-sum((C_4MS_X_T180_day3-C_4MS_T180_day3E).^2+
(C_HYD_X_T180_day3-C_HYD_T180_day3E).^2+
(C_C18_X_T180_day3-mean(C_C18_X_T180_day3)).^2);

Residual_4MS_T180_day3=C_4MS_X_T180_day3-C_4MS_T180_day3E;
Residual_HYD_T180_day3=C_HYD_X_T180_day3-C_HYD_T180_day3E;
Residual_C18_T180_day3=C_C18_X_T180_day3-C_C18_T180_day3E;
Residual_4MS_T180_day3 = C_4MS_X_T180_day3 - mean(C_4MS_X_T180_day3); 
Residual_HYD_T180_day3 = C_HYD_X_T180_day3 - mean(C_HYD_X_T180_day3); 
Residual_C18_T180_day3 = C_C18_X_T180_day3 - mean(C_C18_X_T180_day3);

R2_4MS_T200_day2 = 1 - sum((C_4MS_X_T200_day2 - C_4MS_T200_day2E).^2) / sum((C_4MS_X_T200_day2 - mean(C_4MS_X_T200_day2)).^2); 
R2_HYD_T200_day2 = 1 - sum((C_HYD_X_T200_day2 - C_HYD_T200_day2E).^2) / sum((C_HYD_X_T200_day2 - mean(C_HYD_X_T200_day2)).^2); 
R2_C18_T200_day2 = 1 - sum((C_C18_X_T200_day2 - C_C18_T200_day2E).^2) / sum((C_C18_X_T200_day2 - mean(C_C18_X_T200_day2)).^2);

Residual_4MS_T200_day2 = C_4MS_X_T200_day2 - C_4MS_T200_day2E; 
Residual_HYD_T200_day2 = C_HYD_X_T200_day2 - C_HYD_T200_day2E; 
Residual_C18_T200_day2 = C_C18_X_T200_day2 - C_C18_T200_day2E;

R2_4MS_T250_day2 = 1 - sum((C_4MS_X_T250_day2 - C_4MS_T250_day2E).^2) / sum((C_4MS_X_T250_day2 - mean(C_4MS_X_T250_day2)).^2); 
R2_HYD_T250_day2 = 1 - sum((C_HYD_X_T250_day2 - C_HYD_T250_day2E).^2) / sum((C_HYD_X_T250_day2 - mean(C_HYD_X_T250_day2)).^2); 
R2_C18_T250_day2 = 1 - sum((C_C18_X_T250_day2 - C_C18_T250_day2E).^2) / sum((C_C18_X_T250_day2 - mean(C_C18_X_T250_day2)).^2);

Residual_4MS_T250_day2 = C_4MS_X_T250_day2 - C_4MS_T250_day2E; 
Residual_HYD_T250_day2 = C_HYD_X_T250_day2 - C_HYD_T250_day2E; 
Residual_C18_T250_day2 = C_C18_X_T250_day2 - C_C18_T250_day2E;
\[ R_{2,4MS_{T250_{day3}}} = 1 - \frac{\text{sum}(C_{4MS_{X_{T250_{day3}}}} - C_{4MS_{T250_{day3}E}})^2}{\text{sum}(C_{4MS_{X_{T250_{day3}}}} - \text{mean}(C_{4MS_{X_{T250_{day3}}}}))^2}; \]

\[ R_{2,HYD_{T250_{day3}}} = 1 - \frac{\text{sum}(C_{HYD_{X_{T250_{day3}}}} - C_{HYD_{T250_{day3}E}})^2}{\text{sum}(C_{HYD_{X_{T250_{day3}}}} - \text{mean}(C_{HYD_{X_{T250_{day3}}}}))^2}; \]

\[ R_{2,C_{18_{T250_{day3}}}} = 1 - \frac{\text{sum}(C_{C_{18_{X_{T250_{day3}}}}}} - C_{C_{18_{T250_{day3}E}})^2}{\text{sum}(C_{C_{18_{X_{T250_{day3}}}}}} - \text{mean}(C_{C_{18_{X_{T250_{day3}}}}})^2); \]

\[ R_{2,T_{250_{day3}}} = 1 - \frac{\text{sum}(C_{4MS_{X_{T250_{day3}}}} - C_{4MS_{T250_{day3}E}})^2 + (C_{HYD_{X_{T250_{day3}}}} - C_{HYD_{T250_{day3}E}})^2 + (C_{C_{18_{X_{T250_{day3}}}}}} - C_{C_{18_{T250_{day3}E}})^2}{\text{sum}(C_{4MS_{X_{T250_{day3}}}} - \text{mean}(C_{4MS_{X_{T250_{day3}}}}))^2 + (C_{HYD_{X_{T250_{day3}}}} - \text{mean}(C_{HYD_{X_{T250_{day3}}}}))^2 + (C_{C_{18_{X_{T250_{day3}}}}}} - \text{mean}(C_{C_{18_{X_{T250_{day3}}}}})^2); \]

\[ \text{Residual}_{4MS_{T250_{day3}}} = C_{4MS_{X_{T250_{day3}}}} - C_{4MS_{T250_{day3}E}}; \]

\[ \text{Residual}_{HYD_{T250_{day3}}} = C_{HYD_{X_{T250_{day3}}}} - C_{HYD_{T250_{day3}E}}; \]

\[ \text{Residual}_{C_{18_{T250_{day3}}}} = C_{C_{18_{X_{T250_{day3}}}}}} - C_{C_{18_{T250_{day3}E}}}; \]

\[ R_{2,cC_{6ene_{T150_{day2}}}} = 1 - \frac{\text{sum}(C_{cC_{6ene_{X_{T150_{day2}}}}}} - C_{cC_{6ene_{T150_{day2}E}})^2}{\text{sum}(C_{cC_{6ene_{X_{T150_{day2}}}}}} - \text{mean}(C_{cC_{6ene_{X_{T150_{day2}}}}})^2); \]

\[ R_{2,cC_{6ene_{T180_{day2}}}} = 1 - \frac{\text{sum}(C_{cC_{6ene_{X_{T180_{day2}}}}}} - C_{cC_{6ene_{T180_{day2}E}})^2}{\text{sum}(C_{cC_{6ene_{X_{T180_{day2}}}}}} - \text{mean}(C_{cC_{6ene_{X_{T180_{day2}}}}})^2); \]

\[ R_{2,cC_{6ene_{T200_{day2}}}} = 1 - \frac{\text{sum}(C_{cC_{6ene_{X_{T200_{day2}}}}}} - C_{cC_{6ene_{T200_{day2}E}})^2}{\text{sum}(C_{cC_{6ene_{X_{T200_{day2}}}}}} - \text{mean}(C_{cC_{6ene_{X_{T200_{day2}}}}})^2); \]

\[ R_{2,cC_{6ene_{T250_{day2}}}} = 1 - \frac{\text{sum}(C_{cC_{6ene_{X_{T250_{day2}}}}}} - C_{cC_{6ene_{T250_{day2}E}})^2}{\text{sum}(C_{cC_{6ene_{X_{T250_{day2}}}}}} - \text{mean}(C_{cC_{6ene_{X_{T250_{day2}}}}})^2); \]

\[ \text{Residual}_{cC_{6ene_{T150_{day2}}}} = C_{cC_{6ene_{X_{T150_{day2}}}}}} - C_{cC_{6ene_{T150_{day2}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T180_{day2}}}} = C_{cC_{6ene_{X_{T180_{day2}}}}}} - C_{cC_{6ene_{T180_{day2}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T200_{day2}}}} = C_{cC_{6ene_{X_{T200_{day2}}}}}} - C_{cC_{6ene_{T200_{day2}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T250_{day2}}}} = C_{cC_{6ene_{X_{T250_{day2}}}}}} - C_{cC_{6ene_{T250_{day2}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T150_{day3}}}} = C_{cC_{6ene_{X_{T150_{day3}}}}}} - C_{cC_{6ene_{T150_{day3}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T180_{day3}}}} = C_{cC_{6ene_{X_{T180_{day3}}}}}} - C_{cC_{6ene_{T180_{day3}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T200_{day3}}}} = C_{cC_{6ene_{X_{T200_{day3}}}}}} - C_{cC_{6ene_{T200_{day3}E}}}; \]

\[ \text{Residual}_{cC_{6ene_{T250_{day3}}}} = C_{cC_{6ene_{X_{T250_{day3}}}}}} - C_{cC_{6ene_{T250_{day3}E}}}; \]
figure;

%T=150 day2
subplot(2,4,1)
plot(M,C_4MS_X_T150_day2,'bo',M,C_HYD_X_T150_day2,'md',
    M,C_C18_X_T150_day2,'r+',m,C_4MS_T150_day2,'b-',
    m,C_HYD_T150_day2,'m-',m,C_C18_T150_day2,'r-',
    'LineWidth',1.1)
legend('4-MS','HYD','C18',1)
title(T=150$^\circ$C)
ylabel({'Day 2'; 'Concentration, M'})

%T=180 day2
subplot(2,4,2)
plot(M,C_4MS_X_T180_day2,'bo',M,C_HYD_X_T180_day2,'md',
    M,C_C18_X_T180_day2,'r+',m,C_4MS_T180_day2,'b-',
    m,C_HYD_T180_day2,'m-',m,C_C18_T180_day2,'r-',
    'LineWidth',1.1)
title(T=180$^\circ$C)

%T=200 day2
subplot(2,4,3)
plot(M,C_4MS_X_T200_day2,'bo',M,C_HYD_X_T200_day2,'md',
    M,C_C18_X_T200_day2,'r+',m,C_4MS_T200_day2,'b-',
    m,C_HYD_T200_day2,'m-',m,C_C18_T200_day2,'r-',
    'LineWidth',1.1)
title(T=200$^\circ$C)

%T=250 day2
subplot(2,4,4)
plot(M_250,C_4MS_X_T250_day2,'bo',M_250,C_HYD_X_T250_day2,'md',
    M_250,C_C18_X_T250_day2,'r+',m_250,C_4MS_T250_day2,'b-',
    m_250,C_HYD_T250_day2,'m-',m_250,C_C18_T250_day2,'r-',
    'LineWidth',1.1)
title(T=250$^\circ$C)

%T=150 day3
subplot(2,4,5)
plot(M,C_4MS_X_T150_day3,'bo',M,C_HYD_X_T150_day3,'md',
    M,C_C18_X_T150_day3,'r+',m,C_4MS_T150_day3,'b-',
    m,C_HYD_T150_day3,'m-',m,C_C18_T150_day3,'r-',
    'LineWidth',1.1)
ylabel({'Day 3'; 'Concentration, M'})
xlabel('Catalyst mass, g')

%T=180 day3
subplot(2,4,6)
plot(M,C_4MS_X_T180_day3,'bo',M,C_HYD_X_T180_day3,'md',
    M,C_C18_X_T180_day3,'r+',m,C_4MS_T180_day3,'b-',
    m,C_HYD_T180_day3,'m-',m,C_C18_T180_day3,'r-',
    'LineWidth',1.1)
xlabel('Catalyst mass, g')
plot(M_cC6ene_X_T150_day3,'bo',M_cC6_X_T150_day3,'md',... 
  m_cC6ene_T150_day3,'b-',m_cC6_T150_day3,'m-','MarkerSize',7,... 
  'LineWidth',1.1) 
title('T=150C') 
ylabel({'Day 2';'Concentration, M'})

%T=180 day3 
subplot(2,4,6) 
plot(M_cC6ene_X_T180_day3,'bo',M_cC6_X_T180_day3,'md',... 
  m_cC6ene_T180_day3,'b-',m_cC6_T180_day3,'m-','MarkerSize',7,... 
  'LineWidth',1.1) 
title('T=180C')

%T=200 day3 
subplot(2,4,7) 
plot(M_cC6ene_X_T200_day3,'bo',M_cC6_X_T200_day3,'md',... 
  m_cC6ene_T200_day3,'b-',m_cC6_T200_day3,'m-','MarkerSize',7,... 
  'LineWidth',1.1) 
title('T=200C')

%T=250 day3 
subplot(2,4,8) 
plot(M_250_cC6ene_X_T250_day3,'bo',M_250_cC6_X_T250_day3,'md',... 
  m_cC6ene_T250_day3,'b-',m_cC6_T250_day3,'m-','MarkerSize',7,... 
  'LineWidth',1.1) 
title('T=250C')

fprintf('k1_150_day2= %.5fn', k1_150_day2); 
fprintf('k1_180_day2= %.5fn', k1_180_day2); 
fprintf('k1_200_day2= %.5fn', k1_200_day2); 
fprintf('k1_250_day2= %.5fn', k1_250_day2); 

fprintf('k2_150_day2= %.5fn', k2_150_day2); 
fprintf('k2_180_day2= %.5fn', k2_180_day2); 
fprintf('k2_200_day2= %.5fn', k2_200_day2); 
fprintf('k2_250_day2= %.5fn', k2_250_day2); 

fprintf('k1_150_day3= %.5fn', k1_150_day3); 
fprintf('k1_180_day3= %.5fn', k1_180_day3); 
fprintf('k1_200_day3= %.5fn', k1_200_day3); 
fprintf('k1_250_day3= %.5fn', k1_250_day3); 

fprintf('k2_150_day3= %.5fn', k2_150_day3); 
fprintf('k2_180_day3= %.5fn', k2_180_day3); 
fprintf('k2_200_day3= %.5fn', k2_200_day3); 
fprintf('k2_250_day3= %.5fn', k2_250_day3); 

fprintf('R2_T150_day2_4MS = %.5fn', R2_4MS_T150_day2 ); 
fprintf('R2_T150_day2_HYD = %.5fn', R2_HYD_T150_day2 ); 
fprintf('R2_T150_day2_C18 = %.5fn', R2_C18_T150_day2 );
fprintf('R2_T180_day2_4MS = %.5f\n', R2_4MS_T180_day2);
fprintf('R2_T180_day2_HYD = %.5f\n', R2_HYD_T180_day2);
fprintf('R2_T180_day2_C18 = %.5f\n', R2_C18_T180_day2);

fprintf('R2_T200_day2_4MS = %.5f\n', R2_4MS_T200_day2);
fprintf('R2_T200_day2_HYD = %.5f\n', R2_HYD_T200_day2);
fprintf('R2_T200_day2_C18 = %.5f\n', R2_C18_T200_day2);

fprintf('R2_T250_day2_4MS = %.5f\n', R2_4MS_T250_day2);
fprintf('R2_T250_day2_HYD = %.5f\n', R2_HYD_T250_day2);
fprintf('R2_T250_day2_C18 = %.5f\n', R2_C18_T250_day2);

fprintf('R2_T150_day2 = %.5f\n', R2_T150_day2);
fprintf('R2_T180_day2 = %.5f\n', R2_T180_day2);
fprintf('R2_T200_day2 = %.5f\n', R2_T200_day2);
fprintf('R2_T250_day2 = %.5f\n', R2_T250_day2);

fprintf('R2_T150_day3_4MS = %.5f\n', R2_4MS_T150_day3);
fprintf('R2_T150_day3_HYD = %.5f\n', R2_HYD_T150_day3);
fprintf('R2_T150_day3_C18 = %.5f\n', R2_C18_T150_day3);

fprintf('R2_T180_day3_4MS = %.5f\n', R2_4MS_T180_day3);
fprintf('R2_T180_day3_HYD = %.5f\n', R2_HYD_T180_day3);
fprintf('R2_T180_day3_C18 = %.5f\n', R2_C18_T180_day3);

fprintf('R2_T200_day3_4MS = %.5f\n', R2_4MS_T200_day3);
fprintf('R2_T200_day3_HYD = %.5f\n', R2_HYD_T200_day3);
fprintf('R2_T200_day3_C18 = %.5f\n', R2_C18_T200_day3);

fprintf('R2_T250_day3_4MS = %.5f\n', R2_4MS_T250_day3);
fprintf('R2_T250_day3_HYD = %.5f\n', R2_HYD_T250_day3);
fprintf('R2_T250_day3_C18 = %.5f\n', R2_C18_T250_day3);

fprintf('R2_T150_day3 = %.5f\n', R2_T150_day3);
fprintf('R2_T180_day3 = %.5f\n', R2_T180_day3);
fprintf('R2_T200_day3 = %.5f\n', R2_T200_day3);
fprintf('R2_T250_day3 = %.5f\n', R2_T250_day3);

k1_day2=[k1_150_day2
    k1_180_day2
    k1_200_day2
    k1_250_day2]

k2_day2=[k2_150_day2
    k2_180_day2
    k2_200_day2
    k2_250_day2]

k1_day3=[k1_150_day3
    k1_180_day3
    k1_200_day3
    k1_250_day3]
k2_day3=[k2_150_day3
k2_180_day3
k2_200_day3
k2_250_day3]

kC6_day2=[kC6_150_day2
kC6_180_day2
kC6_200_day2
kC6_250_day2]

kC6_day3=[kC6_150_day3
kC6_180_day3
kC6_200_day3
kC6_250_day3]

R2_4MS_all_day2=1-sum((C_4MS_X_T150_day2-C_4MS_T150_day2E).^2+
(C_4MS_X_T180_day2-C_4MS_T180_day2E).^2+
(C_4MS_X_T200_day2-C_4MS_T200_day2E).^2)/
sum((C_4MS_X_T150_day2-mean(C_4MS_X_T150_day2)).^2+
(C_4MS_X_T180_day2-mean(C_4MS_X_T180_day2)).^2+
(C_4MS_X_T200_day2-mean(C_4MS_X_T200_day2)).^2)

R2_4MS_all_day3=1-sum((C_4MS_X_T150_day3-C_4MS_T150_day3E).^2+
(C_4MS_X_T180_day3-C_4MS_T180_day3E).^2+
(C_4MS_X_T200_day3-C_4MS_T200_day3E).^2)/
sum((C_4MS_X_T150_day3-mean(C_4MS_X_T150_day3)).^2+
(C_4MS_X_T180_day3-mean(C_4MS_X_T180_day3)).^2+
(C_4MS_X_T200_day3-mean(C_4MS_X_T200_day3)).^2)

R2_all_day2=1-sum((C_HYD_X_T150_day2-C_HYD_T150_day2E).^2+
(C_HYD_X_T180_day2-C_HYD_T180_day2E).^2+
(C_HYD_X_T200_day2-C_HYD_T200_day2E).^2)/
sum((C_HYD_X_T150_day2-mean(C_HYD_X_T150_day2)).^2+
(C_HYD_X_T180_day2-mean(C_HYD_X_T180_day2)).^2+
(C_HYD_X_T200_day2-mean(C_HYD_X_T200_day2)).^2)

R2_all_day3=1-sum((C_HYD_X_T150_day3-C_HYD_T150_day3E).^2+
(C_HYD_X_T180_day3-C_HYD_T180_day3E).^2+
(C_HYD_X_T200_day3-C_HYD_T200_day3E).^2)
\[(C_{HYD} \times T_{180\_day3} - C_{HYD} \times T_{180\_day3E})^2 + \ldots + (C_{C18} \times T_{180\_day3} - C_{C18} \times T_{180\_day3E})^2 + \ldots + (C_{4MS} \times T_{200\_day3} - C_{4MS} \times T_{200\_day3E})^2 + \ldots + (C_{HYD} \times T_{200\_day3} - C_{HYD} \times T_{200\_day3E})^2) / \sum((C_{4MS} \times T_{150\_day3} - \text{mean}(C_{4MS} \times T_{150\_day3}))^2 + \ldots + (C_{HYD} \times T_{150\_day3} - \text{mean}(C_{HYD} \times T_{150\_day3}))^2 + \ldots + (C_{C18} \times T_{150\_day3} - \text{mean}(C_{C18} \times T_{150\_day3}))^2 + \ldots + (C_{4MS} \times T_{180\_day3} - \text{mean}(C_{4MS} \times T_{180\_day3}))^2 + \ldots + (C_{HYD} \times T_{180\_day3} - \text{mean}(C_{HYD} \times T_{180\_day3}))^2 + \ldots + (C_{C18} \times T_{180\_day3} - \text{mean}(C_{C18} \times T_{180\_day3}))^2 + \ldots + (C_{4MS} \times T_{200\_day3} - \text{mean}(C_{4MS} \times T_{200\_day3}))^2 + \ldots + (C_{HYD} \times T_{200\_day3} - \text{mean}(C_{HYD} \times T_{200\_day3}))^2 + \ldots + (C_{C18} \times T_{200\_day3} - \text{mean}(C_{C18} \times T_{200\_day3}))^2))\]

\[R_2^{cC6ene\_all\_day2} = 1 - \sum((c_{cC6ene} \times T_{150\_day2} - c_{cC6ene} \times T_{150\_day2E})^2 + \ldots + (c_{cC6ene} \times T_{200\_day2} - c_{cC6ene} \times T_{200\_day2E})^2) / \sum((c_{cC6ene} \times T_{150\_day2} - \text{mean}(c_{cC6ene} \times T_{150\_day2}))^2 + \ldots + (c_{cC6ene} \times T_{200\_day2} - \text{mean}(c_{cC6ene} \times T_{200\_day2}))^2)\]

\[R_2^{cC6ene\_all\_day3} = 1 - \sum((c_{cC6ene} \times T_{150\_day3} - c_{cC6ene} \times T_{150\_day3E})^2 + \ldots + (c_{cC6ene} \times T_{200\_day3} - c_{cC6ene} \times T_{200\_day3E})^2) / \sum((c_{cC6ene} \times T_{150\_day3} - \text{mean}(c_{cC6ene} \times T_{150\_day3}))^2 + \ldots + (c_{cC6ene} \times T_{200\_day3} - \text{mean}(c_{cC6ene} \times T_{200\_day3}))^2)\]
H.2 Objective function code

% This function is used to calculate the objective function for 4-MS reaction
function OBJ=OBJECTIVE_FUN_MLE_Thesis_all_noC18(p, m,C_4MS_X,C_HYD_X,C_C18_X)

C_0=[C_4MS_X(1);C_HYD_X(1)];

% calculating model predictions using current parameters
[Tm,Y]=ode45('ODE_FUN_Thesis_noC18',m,C_0,[],p);

% extracting model predictions
C_4MS =real(abs(Y(:,1)));
C_HYD =real(abs(Y(:,2)));

% calculating objective function
OBJ=sum((C_4MS-C_4MS_X').^2+(C_HYD-C_HYD_X').^2);

% This function is used to calculate the objective function for cyclohexene reactions
function OBJ=OBJECTIVE_FUN_MLE_ThesisC6_all(p, m,C_cC6ene_X,C_cC6_X)

C_0=[C_cC6ene_X(1);C_cC6_X(1)];

% calculating model predictions using current parameters
[Tm,Y]=ode45('ODE_FUN_ThesisC6',m,C_0,[],p);

% extracting model predictions
C_cC6ene=real(abs(Y(:,1)));

% calculating objective function
OBJ=sum((C_cC6ene-C_cC6ene_X').^2);
H.3 Ordinary differential equations code

% This function evaluates the ODE functions for 4-MS reactions parameters
% calculations
function dC = ODE_FUN_Thesis_noC18(m,C,flag,p)

dC=zeros(2,1);

% Extracting model parameters
k1_prime_on_v0=p(1);
k2_prime_on_v0=p(2);

% Extracting species concentrations
C_4MS=C(1);
C_HYD=C(2);

% rate expressions r'/v0
r1_on_v0=k1_prime_on_v0*C_4MS;
r2_on_v0=k2_prime_on_v0*C_4MS^2;

% ODE's for each chemical species
dC(1)=(-r1_on_v0-2*r2_on_v0); % 4MS
dC(2)=r1_on_v0; % HYD

dC(3)=r2_on_v0; % C18


% This function evaluates the ODE functions for 4-MS figures
function dC = ODE_FUN_Thesis(m,C,flag,p)

dC=zeros(3,1);

% Extracting model parameters
k1_prime_on_v0=p(1);
k2_prime_on_v0=p(2);

% Extracting species concentrations
C_4MS=C(1);
C_HYD=C(2);
C_C18=C(3);

% rate expressions r'/v0
r1_on_v0=k1_prime_on_v0*C_4MS;
r2_on_v0=k2_prime_on_v0*C_4MS^2;

% ODE's for each chemical species
dC(1)=(-r1_on_v0-2*r2_on_v0); % 4MS
dC(2)=r1_on_v0; % HYD
dC(3)=r2_on_v0; % C18
% This function evaluates the ODE functions for cyclohexene reaction
function dC = ODE_FUN_ThesisC6(m,C,flag,p)

    dC=zeros(2,1);

    % Extracting model parameters
    kC6_prime_on_v0=p(1);

    % Extracting species concentrations
    C_cC6ene=C(1);

    % Rate expressions r'/v0
    rC6_on_v0=kC6_prime_on_v0*C_cC6ene;

    % ODE's for each chemical species
    dC(1)=-rC6_on_v0;
    dC(2)=rC6_on_v0;
function [x,fval,exitflag,output]=fminsearchbnd3(fun,x0,LB,UB,options,varargin)

% FMINSEARCHBND: FMINSEARCH, but with bound constraints by transformation
% usage: x=FMINSEARCHBND(fun,x0)
% usage: x=FMINSEARCHBND(fun,x0,LB)
% usage: x=FMINSEARCHBND(fun,x0,LB,UB)
% usage: x=FMINSEARCHBND(fun,x0,LB,UB,options)
% usage: x=FMINSEARCHBND(fun,x0,LB,UB.options,p1,p2,...)
% usage: [x,fval,exitflag,output]=FMINSEARCHBND(fun,x0,....)
%
% arguments:
% fun, x0, options - see the help for FMINSEARCH
%
% LB - lower bound vector or array, must be the same size as x0
% % If no lower bounds exist for one of the variables, then
% % supply -inf for that variable.
% % If no lower bounds at all, then LB may be left empty.
% % Variables may be fixed in value by setting the corresponding
% % lower and upper bounds to exactly the same value.
% % UB - upper bound vector or array, must be the same size as x0
% % If no upper bounds exist for one of the variables, then
% % supply +inf for that variable.
% % If no upper bounds at all, then UB may be left empty.
% % Variables may be fixed in value by setting the corresponding
% % lower and upper bounds to exactly the same value.
% % Notes:
% % If options is supplied, then TolX will apply to the transformed
% % variables. All other FMINSEARCH parameters should be unaffected.
% % Variables which are constrained by both a lower and an upper
% % bound will use a sin transformation. Those constrained by
% % only a lower or an upper bound will use a quadratic
% % transformation, and unconstrained variables will be left alone.
% % Variables may be fixed by setting their respective bounds equal.
% % In this case, the problem will be reduced in size for FMINSEARCH.
% % The bounds are inclusive inequalities, which admit the
% % boundary values themselves, but will not permit ANY function
% % evaluations outside the bounds. These constraints are strictly
% % followed.
% If your problem has an EXCLUSIVE (strict) constraint which will
% not admit evaluation at the bound itself, then you must provide
% a slightly offset bound. An example of this is a function which
% contains the log of one of its parameters. If you constrain the
% variable to have a lower bound of zero, then FMINSEARCHBND may
% try to evaluate the function exactly at zero.
%
% Example usage:
% rosen = @(x) (1-x(1)).^2 + 105*(x(2)-x(1)).^2;  
% fminsearch(rosen,[3 3])  % unconstrained
% ans =
%    1.0000    1.0000
% fminsearchbnd(rosen,[3 3],[2 2],[[]])  % constrained
% ans =
%    2.0000    4.0000
% % See test_main.m for other examples of use.
%
% See also: fminsearch, fminspleas
%
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% size checks
xsize = size(x0);
x0 = x0(:);
n=length(x0);

if (nargin<3) || isempty(LB)
    LB = repmat(-inf,n,1);
else
    LB = LB(:);
end
if (nargin<4) || isempty(UB)
    UB = repmat(inf,n,1);
else
    UB = UB(:);
end

if (n~=length(LB)) || (n~=length(UB))
    error 'x0 is incompatible in size with either LB or UB.'
end

% set default options if necessary
if (nargin<5) || isempty(options)
    options = optimset('fminsearch');
% stuff into a struct to pass around
params.args = varargin;
params.LB = LB;
params.UB = UB;
params.fun = fun;
params.n = n;
params.OutputFcn = [];

% 0 --> unconstrained variable
% 1 --> lower bound only
% 2 --> upper bound only
% 3 --> dual finite bounds
% 4 --> fixed variable
params.BoundClass = zeros(n,1);
for i=1:n
    k = isfinite(LB(i)) + 2*isfinite(UB(i));
    params.BoundClass(i) = k;
    if (k==3) && (LB(i)==UB(i))
        params.BoundClass(i) = 4;
    end
end

% transform starting values into their unconstrained surrogates. Check for infeasible starting guesses.
x0u = x0;
k=1;
for i = 1:n
    switch params.BoundClass(i)
    case 1 % lower bound only
        if x0(i)<=LB(i)
            x0u(k) = 0;
        else
            x0u(k) = sqrt(x0(i) - LB(i));
        end
        k=k+1;
    case 2 % upper bound only
        if x0(i)>=UB(i)
            x0u(k) = 0;
        else
            x0u(k) = sqrt(UB(i) - x0(i));
        end
        k=k+1;
    case 3
end
% lower and upper bounds
if x0(i)<=LB(i)
    % infeasible starting value
    x0u(k) = -pi/2;
elseif x0(i)>=UB(i)
    % infeasible starting value
    x0u(k) = pi/2;
else
    x0u(k) = 2*(x0(i)-LB(i))/(UB(i)-LB(i)) - 1;
    % shift by 2*pi to avoid problems at zero in fminsearch
    % otherwise, the initial simplex is vanishingly small
    x0u(k) = 2*pi+asin(max(-1,min(1,x0u(k))));
end

% increment k
k=k+1;

% unconstrained variable. x0u(i) is set.
    x0u(k) = x0(i);

% increment k
k=k+1;

% fixed variable. drop it before fminsearch sees it.
% k is not incremented for this variable.
end

% if any of the unknowns were fixed, then we need to shorten
% x0u now.
if k<=n
    x0u(k:n) = [];
end

% were all the variables fixed?
if isempty(x0u)
    % All variables were fixed. quit immediately, setting the
    % appropriate parameters, then return.

    % undo the variable transformations into the original space
    x = xtransform(x0u,params);

    % final reshape
    x = reshape(x,xsize);

    % stuff fval with the final value
    fval = feval(params.fun,x,params.args{:});

    % fminsearchbnd was not called
    exitflag = 0;

    output.iterations = 0;
output.funcount = 1;
output.algorithm = 'fminsearch';
output.message = 'All variables were held fixed by the applied bounds';

% return with no call at all to fminsearch
return
end

% Check for an outputfcn. If there is any, then substitute my
% own wrapper function.
if ~isempty(options.OutputFcn)
    params.OutputFcn = options.OutputFcn;
    options.OutputFcn = @outfun_wrapper;
end

% now we can call fminsearch, but with our own
% intra-objective function.
[xu,fval,exitflag,output] = fminsearch(@intrafun,x0u,options,params);

% undo the variable transformations into the original space
x = xtransform(xu,params);

% final reshape
x = reshape(x,xsize);

% Use a nested function as the OutputFcn wrapper
function stop = outfun_wrapper(x,varargin);
% we need to transform x first
xtrans = xtransform(x,params);

% then call the user supplied OutputFcn
stop = params.OutputFcn(xtrans,varargin{1:(end-1)});
end
end% mainline end

% ===============
% ========= begin subfunctions =========
% ===============

function fval = intrafun(x,params)
% transform variables, then call original function

% transform
xtrans = xtransform(x,params);

% and call fun
fval = feval(params.fun,xtrans,params.args{:});
end% sub function intrafun end
function xtrans = xtransform(x, params)
% converts unconstrained variables into their original domains

xtrans = zeros(1, params.n);
% k allows some variables to be fixed, thus dropped from the % optimization.
k=1;
for i = 1: params.n
    switch params.BoundClass(i)
        case 1
            % lower bound only
            xtrans(i) = params.LB(i) + x(k).^2;
            k=k+1;
        case 2
            % upper bound only
            xtrans(i) = params.UB(i) - x(k).^2;
            k=k+1;
        case 3
            % lower and upper bounds
            xtrans(i) = (sin(x(k))+1)/2;
            xtrans(i) = xtrans(i)*(params.UB(i) - params.LB(i)) + params.LB(i);
            % just in case of any floating point problems
            xtrans(i) = max(params.LB(i), min(params.UB(i), xtrans(i)));
            k=k+1;
        case 4
            % fixed variable, bounds are equal, set it at either bound
            xtrans(i) = params.LB(i);
        case 0
            % unconstrained variable.
            xtrans(i) = x(k);
            k=k+1;
    end
end
end
% sub function xtransform end