TRANSFORMATION OF ACETONE AND ISOPROPANOL TO HYDROCARBONS USING HZSM-5 CATALYST

A Thesis

by

SEBASTIAN TACO VASQUEZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2009

Major Subject: Chemical Engineering

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Approved by:

Chair of Committee, Mark Holtzapple
Committee Members, Kenneth Hall
Cady Engler
Head of Department, Michael Pishko

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ABSTRACT

Transformation of Acetone and Isopropanol to

Hydrocarbons Using HZSM-5 Catalyst. (December 2009)

Sebastian Taco Vasquez, B.S., Escuela Politécnica Nacional;

Chair of Advisory Committee: Dr. Mark T. Holtzapple

This research describes the production of hydrocarbons from acetone and isopropanol produced by the MixAlco process. The MixAlco process has two types of products: acetone and isopropanol. The effect of the temperature, weight hourly space velocity (WHSV), type of catalyst, feed composition, and pressure are studied.

For the isopropanol reaction, the following conditions were used: HZSM-5 (280), 1 atm, 300–410°C, and 0.5–11.5 h^{-1}, respectively. The temperature and WHSV affect the average carbon number of the reaction products. A product similar to commercial gasoline was obtained at T = 320 °C and WHSV= 1.3 to 2.7 h^{-1}. Also, at these conditions, the amount of light hydrocarbons (C1–C4) is low.

For the acetone reaction, the following conditions were used: HZSM-5 with silica alumina ratio (Si/Al) 80 and 280 mol silica/mol alumina, 1–7.8 atm, 305–415°C, 1.3–11.8 h^{-1}, and hydrogen acetone ratio 0–1 mol H_2 /mol acetone. The conversion on HZSM-5 (80) was higher than HZSM-5 (280); however, for HZM–5 (80) the production of light hydrocarbons (C1–C4) was more abundant than (280), and it formed less coke.

For acetone, the effect of high pressure (P = 7.8 atm) was evaluated. At high pressure, the conversion was lower than at atmospheric pressure. HZSM-5 (280) rapidly deactivated, and the amount of light hydrocarbons (C1–C4) increased.

For acetone, co-feeding hydrogen inhibited coke formation and decreased the amount of light hydrocarbons (C1–C4).

To My Lord and Savior Jesus Christ
"Every good and perfect gift is from above, coming down from the Father of the heavenly lights" James 1:17.

ACKNOWLEDGEMENTS

I especially want to thank my advisor, Dr. Mark Holtzapple, for his guidance during my studies at Texas A&M. Under his supervision, he has encouraged me so much. I admire him for his wide understanding of science and technology, and also his kindness and sincerity. As well, I admire his perseverance and his commitment to his dream of changing waste materials into fuels.

I was delighted to interact with Dr. Jubo Zhang. He was always accessible and willing to help me with this project. He has provided assistance in numerous ways such as fixing the equipment, suggesting new ideas for the project, and providing support. As well, during all this time, we have become good friends and I am grateful that I could meet this extraordinary person.

I want to express my gratitude to the Fulbright Program, which supported me financially and gave me the opportunity to come to the United States to pursue my graduate studies

I would like to thank my thesis committee members Dr. Ken Hall and Dr. Cady Engler for their helpful comments and suggestions.

Dr. Cesar Granda and Gary Luce deserve special thanks. They have been actively involved in this project and their comments were of great value. In particular, they were involved with suggestions for future research.

I am grateful for all the members of my laboratory group. They have always been kind and willing to help me at all times. I also want to thank Diego Cristancho for his help setting up the equipment and his friendship.

I am forever indebted to my parents and my sister for their understanding, endless patience, and encouragement when it was most required. I am also grateful to my mother Rina who encouraged me and cared for me all my life.

Furthermore, Pastor Clyde Wilton has always been a constant source of encouragement during my graduate studies. “The ways of the Lord are always the best”

and “love is always the superior way” are among his teachings that gave me a new perspective on life.

Last, but not least, thanks be to my Lord Jesus Christ. He, who through his spirit, gave me strength and peace during all my life. This thesis would not have been possible unless God’s mercy and love were upon me. May my Lord Jesus Christ be praised, honored, and loved for all eternity.

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CHAPTER I

INTRODUCTION

The high global demand for fuels and the depletion of fossil fuels have motivated research into renewable sources of fuels. Biomass is one of the most abundant and sustainable resources in the world. At Texas A&M University, Dr. Mark Holtzapple's research group has been working extensively for more than 20 years to obtain fuels from biomass. Some biomass feedstocks studied in our group include municipal solid waste, animal manure, and energy crops. The new technology developed by the Holtzapple group is called the MixAlco Process (Figure 1.1), which uses the following steps: pretreatment, fermentation, descumming, dewatering, ketonization, alcoholization, and oligomerization. Depending how many steps are employed, the final product of this process is ketones, alcohols, or hydrocarbons.

This thesis assesses the oligomerization process, the last step of the MixAlco process. The objective is to produce hydrocarbons similar to commercial gasoline using a solid catalyst in a packed-bed reactor.

Figure 1.1 shows that either alcohols or ketones can be transformed into hydrocarbons. Zeolite solid-acid catalyst HZSM-5 transforms either alcohols or ketones into hydrocarbons and is the focus of this thesis.

In the MixAlco process, isopropanol is the most abundant alcohol and acetone is the most abundant ketone; therefore, they are the focus of this thesis. The objective of this research is to define the conditions of isopropanol and acetone reaction in order to obtain a mixture of hydrocarbons similar to commercial gasoline.

This thesis follows the style of Bioresource Technology.

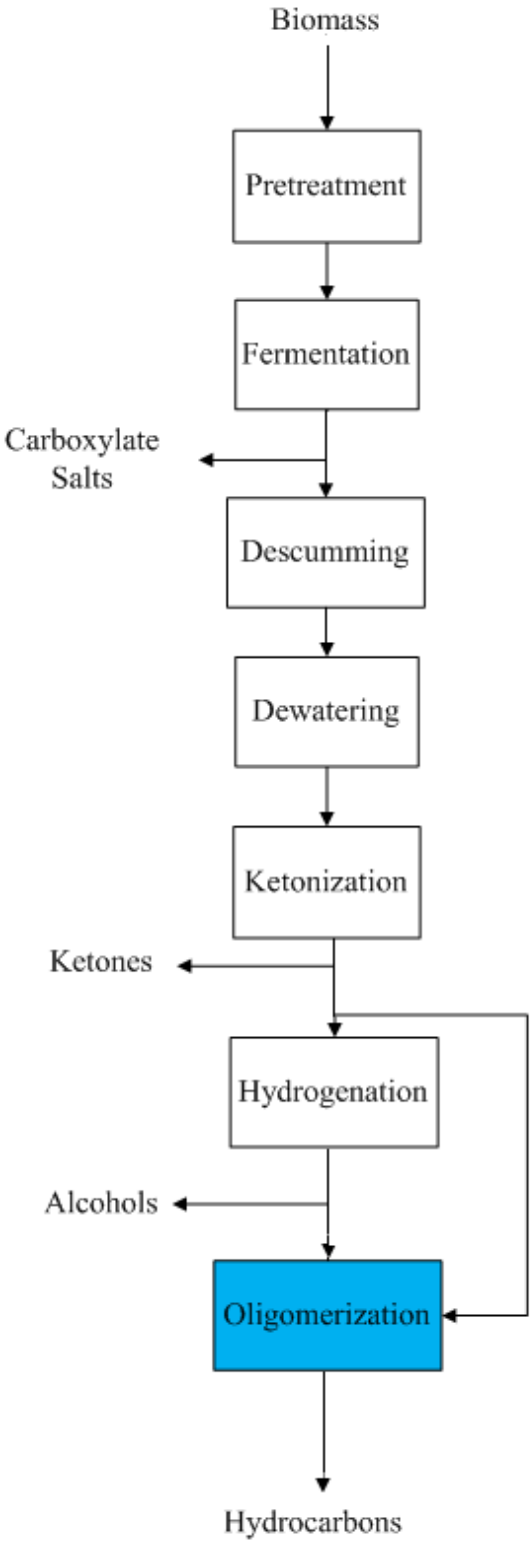

Figure 1.1. MixAlco process.

This thesis has six chapters:

Chapter I is the introduction.

Chapter II describes the theoretical background and previous work on the reaction of acetone and isopropanol over HZSM-5 catalyst. It shows experimental results from previous studies and proposed mechanisms for the reaction of isopropanol and acetone.

Chapter III describes the experimental procedure and equipment for this research.

Chapter IV focuses on the isopropanol reaction and investigates the effect of temperature and weight hourly space velocity (WHSV). The catalyst was HZSM-5 (280) at 1 atm.

Chapter V focuses on the acetone reaction and investigates effects of temperature and WHSV using HZSM-5 (80) and HZSM-5 (280) at 1 atm and 7.8 atm (absolute). Chapter V also shows the effect of co-feeding hydrogen with acetone into the reactor. All the catalysts studied for the acetone reaction are commercially available.

Chapter VI presents the conclusions and recommendation for this research.

Chapter VII shows future studies for this research.

CHAPTER II

LITERATURE REVIEW

2.1 Biomass to Hydrocarbons

Hydrocarbons can be produced from biomass using several platforms: sugar, thermochemical, and carboxylate.

The sugar platform hydrolyzes biomass into sugars by adding enzymes. This process requires sterility because contaminants will consume the sugars. The sugars are fermented to alcohols, which can be converted to hydrocarbons using zeolite catalyst.

The thermochemical platform converts biomass into carbon monoxide and hydrogen, which react to form hydrocarbons using the Fisher-Tropsch process, a catalytic heterogeneous reaction that uses a cobalt catalyst.

The carboxylate platform ferments biomass into carboxylic acids, which are neutralized using a buffer (e.g., $CaCO_3$). Then, the calcium carboxylate salts are transformed into ketones by heating (~440 °C) under vacuum. The ketones can be hydrogenated to alcohols. The ketones or alcohols are converted into hydrocarbons via oligomerization (Figure 1.1).

2.2 Alcohols to Hydrocarbons over HZSM-5 Catalyst

2.2.1 HZSM-5 Catalyst

ZSM-5 is an aluminosilicate zeolite catalyst composed of AlO_4 and SiO_4 tetrahedra interconnected through shared oxygen atoms (Figure 2.1). The aluminum ion (charge 3+) and a silicon ion (charge 4+) interconnect with oxygen atoms and require the addition of a proton. This additional proton gives the zeolite a high level of acidity, which is responsible for its activity. Figure 2.1a shows ammonium ZSM-5, which is the commercial ZSM-5 catalyst. Above 300°C, NH_4^+ ZSM-5 loses ammonia and forms H^+ZSM-5.

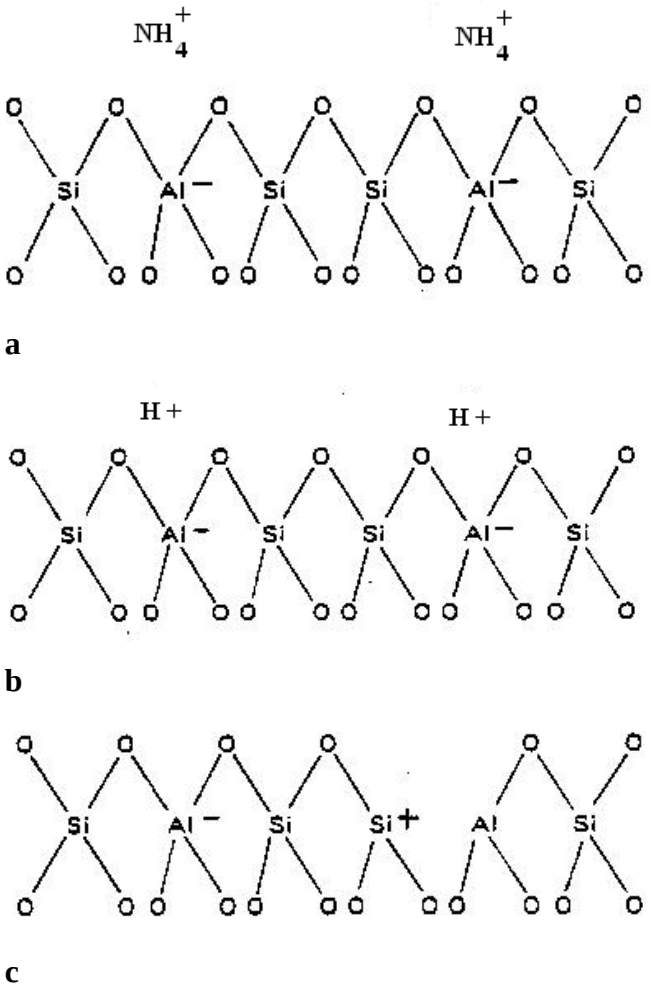

Figure 2.1. Structure of ZSM-5. (**a**) Structure of NH_4^+ZSM-5. (**b**) Structure of NH_4^+ZSM-5. (**c**) Dehydration of HZSM-5 to Lewis Acid.

ZSM-5 has two types of acidity: Bronsted (Figure 2.1b) or Lewis (Figure 2.1c). The dehydration of a Bronsted acid site produces a Lewis acid site. In the production of hydrocarbons, the contribution of the Lewis acidity is considered to be negligible compared to Bronsted acidity. In 1980, Anderson et al. showed that the active sites involved in the conversion of methanol on zeolites are Bronsted acids, not Lewis acids.

The catalyst HZSM-5 is characterized by the silica alumina ratio. For example ZSM-5 (80) has 80 moles of silica per mole of alumina. Larger Si/Al ratios are less acidic, and hence less reactive.

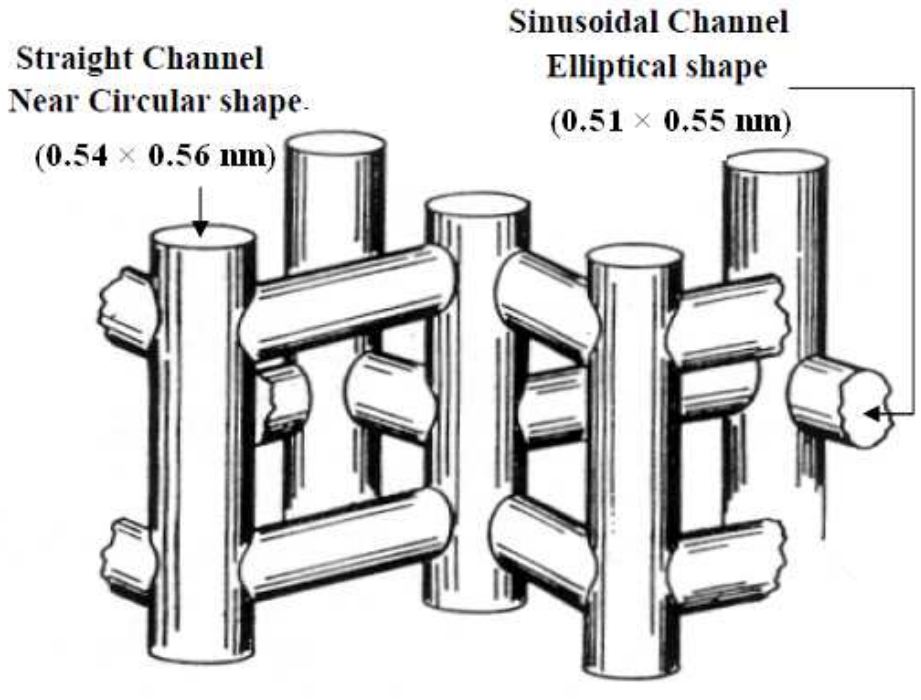

Figure 2.2. Pore structure of HZSM-5 (Figure from Dent and Smith, 1958).

Figure 2.2 shows that HZSM-5 zeolite contains two perpendicularly intersecting channel systems: (1) sinusoids with crosssections of approximately 0.51 × 0.55 nm, and (2) straight channels with cross sections of 0.54 × 0.56 nm.

Transformation of alcohols to hydrocarbons over HZSM-5 has been studied since the development of MTO (methanol-to-olefins), invented by Mobil Corporation in 1977. This technology was a breakthrough that produced gasoline from methanol. This process capitalized on existing technology that transformed coal and natural gas into methanol.

Methanol-to-olefins is a heterogeneous catalytic process. In 1977, Chang and Silvestri published the first experimental results showing the effectiveness of catalyst HZSM-5 for converting methanol to gasoline.

Chang and Silvestri (1977) studied the effect of temperature, pressure, and space velocity on the conversion and selectivity of the products. Figure 2.3 shows the product distribution and conversion at different space velocities at 371 °C.

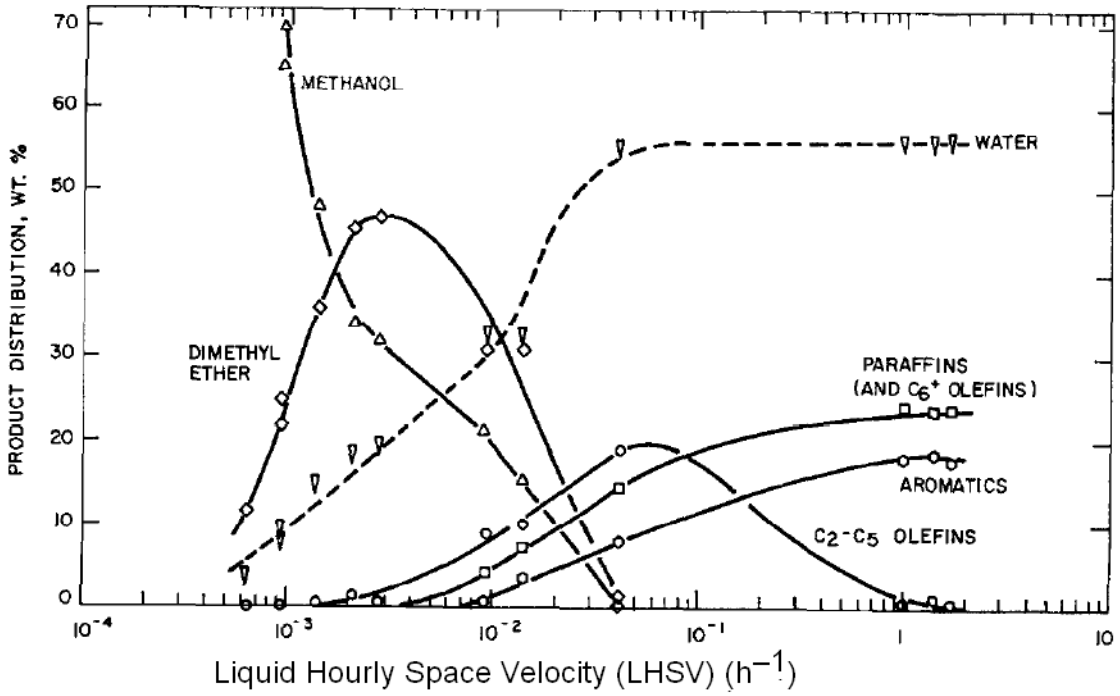

Figure 2.3. Reaction path for methanol conversion to hydrocarbons at T = 371°C (LHSV is liquid hourly space velocity and is equal to the feed rate over catalyst volume, Figure from Chang and Silvestri, 1977).

Figure 2.3 gives insights into the reaction mechanism of methanol. According to Chang and Silvestri (1977), the methanol reaction path follows:

$$2CH_3OH \xrightarrow{-H_2O} CH_3OCH_3 \xrightarrow{-H_2O} C2-C5 \longrightarrow \begin{matrix}\text{paraffins}\\ \text{aromatics}\\ \text{cycloparaffins}\\ C6^{+}\text{ olefins}\end{matrix}$$

It is noteworthy that intermediate products are C2 to C5 olefins produced before the larger reaction molecules.

Since HZSM-5 was tested for methanol, other alcohols have been investigated. In 1987, Fuhse and Friedhelm presented results of different alcohols (e.g., ethanol, *n*-

propanol, isopropanol, *n*-butanol, and hexanol) over HZSM-5. The silica alumina ratio was 65 mol silica/mol alumina, WHSV = 0.37 h^{-1}, and T = 400 °C. Some of their results are shown in Table 2.1.

The results from Table 2.1 show that for all alcohols tested, more gaseous products are produced than liquids. As well, in all cases except for ethanol, the most abundant reaction product is propene. In a graphic form, Figure 2.4 shows the results of Table 2.1. The product distribution is similar for all alcohols, which may result because all these alcohols undergo a similar reaction mechanism.

Table 2.1 Product distribution of some alcohols at WHSV = 0.37 h^{-1}, T = 400 °C (Fuhse and Friedhelm, 1987)

	Ethanol (wt%)	*n*-Propanol (wt%)	Isopropanol (wt%)	*n*-Butanol (wt%)	Hexan-1-ol (wt%)
C2	31.9	6.5	6.6	6.6	6.9
C3	8.4	12.7	12.5	11.9	10
*C3	15.4	17.8	17.8	16.5	14.9
C4	11.9	16.8	16.6	16.6	15.9
*C4	13.4	15.5	15.5	14.9	13.8
$C5^{+}$	12.2	13.9	14.6	12.9	13.9
**C6	0	1.5	1.6	1.8	1.9
**C7	4.4	7.6	7.4	9.4	8.9
$**C8^{+}$	2.4	7.7	7.4	9.4	13.8
Gas	81	69.3	69	66.5	61.5
Liquid	19	30.7	31	33.5	38.5

* = Olefins; ** = Aromatics

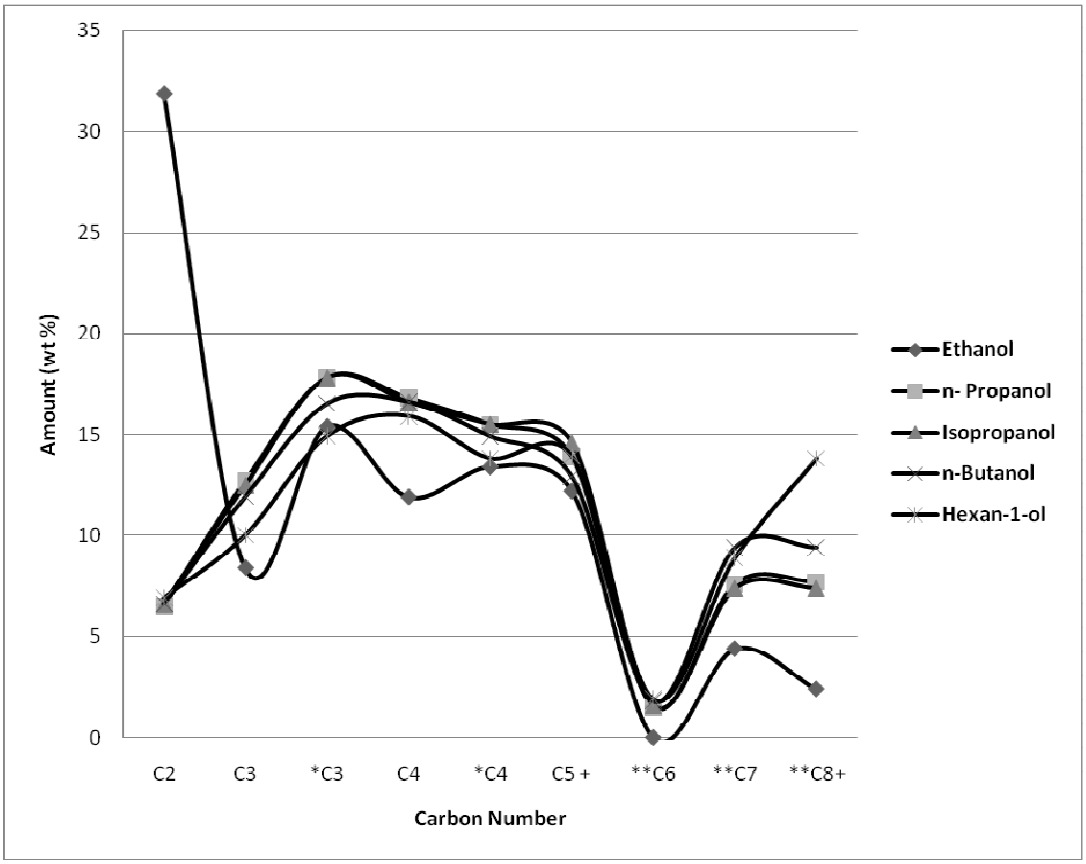

Figure 2.4. Carbon product distribution for different alcohols over HZSM-5 (65) at WHSV = 0.37 h–1, T = 400 °C, P = 1 atm (absolute). (* = Olefins; ** = Aromatics; Figure adapted from Fuhse and Friedhelm, 1987).

After Fuhse and Friedhelm (1987), more studies were done for isopropanol over HZSM-5. Gayubo et al. (2004b) presented a broad study of the isopropanol reaction, which provides insights into the reaction mechanism. According to Gayubo et al. (2004b), the reaction of isopropanol over HZSM-5 is mainly dehydration to propene, which forms hydrocarbons above 250 °C. Figure 2.5 shows the reaction mechanism of isopropanol over HZSM-5.

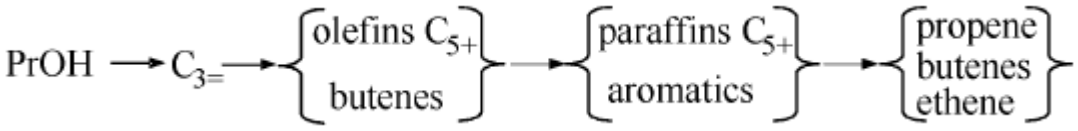

Figure 2.5. Reaction path for isopropanol (Gayubo et al. 2004b).

Table 2.2 Effect of temperature on reaction products for isopropanol over HZSM-5. (adapted from Gayubo et al. 2004b).

T (°C)	Effect on reaction products	Reaction type
200–250	Propene is the only product	Dehydration
250–310	Butenes and $C5^+$ olefins (hexene)	Propene dimerization
310–400	Propene (increases again) Paraffins $C5^+$ and aromatics	Oligomerization to large molecules
410 +	Ethene, butenes and propenes	Cracking of heavy molecules

Gayubo et al. 2004b also reported the effect of temperature (200 to 450°C) for isopropanol reaction over HZSM-5 (see Table 2.2).

Gayubo et al. 2004b also investigated for the effect of weight hourly space velocity (WHSV = 3 to 40 h^{-1}). WHSV is the mass ratio of feedstock rate over the mass of catalyst. Figure 2.5 shows the reaction path of isopropanol when WHSV changes. At very high WHSV = 40 h^{-1}, propene is the most abundant reaction produce. However, when WHSV decreases, the amount of olefins, aromatics, and paraffins increases. At very low WHSV (3 h^{-1}), ethane, propene, and butene are produced again because heavy molecules (e.g., paraffins and aromatics) crack.

According to Gayubo et al. (2004b), propene never disappears from the reaction products, and the deactivation of HZSM-5 is low for alcohols.

2.3 Reaction of Acetone over HZSM-5

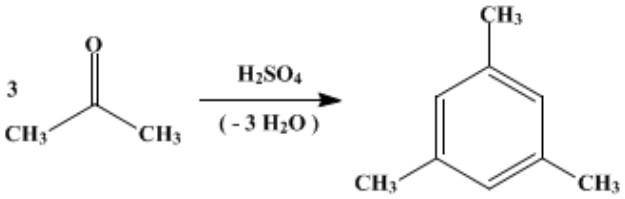

Figure 2.6. Aldol condensation of acetone to mesitylene.

Although isopropanol and acetone differ by only two hydrogen atoms in their molecules, their reaction mechanisms are very different.

According to Chang (1977), with HZSM-5, acetone undergoes classic acid-catalyzed condensation to mesitylene (also called aldol condensation), which occurs when acetone contacts any acid. For example, when acetone contacts sulfuric acid for a long time, it forms an aldol. If the temperature is high enough, the aldol forms mesitylene (see Figure 2.6).

Because zeolites have catalytic acid sites in their structure, the reaction of acetone with sulfuric acid is similar to the reaction of acetone with zeolite. Both the zeolite (HZSM-5) and the acid catalyze the reaction. However, according to Salvapatini et al. (1989), the catalytic self-condensation of acetone is very complex and has numerous products, including diacetone alcohol, mesityl oxide, phorone, mesitylene, isophorone, and 3,5-xilenol. The product spectrum depends on the experimental conditions. Experimental conditions, such as temperature, pressure and catalyst, also determine the reaction products obtained from acetone (Salvapati et al. 1989).

Chang and Silvestri (1977) pioneered the oligomerization of acetone on HZSM-5 catalyst using a packed-bed reactor for their experiments. They studied temperatures from 250 to 400 °C using WHSV = 8 h^{-1} at 1 atm (absolute)

Table 2.3 shows the product distribution of acetone reaction presented by Chang and Silvestri (1977). The conversion increased from 3.9% (250 °C) to 95.3% (400 °C). The amount of isobutene decreased significantly with increased temperature from 83.3%

(329 °C) to 3.6% (399°C). This may be attributed to the oligomerization of isobutene into aromatics according to the study by Salvapati et al. (1989). It is noteworthy that the most abundant hydrocarbon at high temperatures (399°C) is xylene. It is also notable, that among all the reaction liquid products ($C6^+$), most are aromatics.

Table 2.3 Product distribution of acetone reaction over HZSM-5 catalyst (Chang and Silvestri, 1977).

Reaction Conditions				
T (°C)	250	288	329	399
LHSV (h^{-1})	8.0	8.0	8.0	8.0
Conversion (%)	3.9	6.0	24.5	95.3
Carbon Selectivity, (%)				
Diacetone	3.5	2.9	0.1	–
Mesitul oxide	27.3	19.7	1.2	–
Isophorone	–	<0.1	5.3	–
Other O-compounds	6.0	15.0	<0.1	–
CO + CO_2	–	0.7	10.0	6.1
Hydrocarbons	63.2	61.2	83.4	93.9
Hydrocarbon Distribution (wt%)			–	
Methane	–	–	0.2	0.1
Ethane	–	–	0.4	0.2
Ethylene	<0.1	<0.1	1.2	2.4
Propane		0.3	1.9	4.2
Propylene	2.5	3.8	4.2	5.2
i-Butane	–	–	0.1	3.9
n-Butane	–	–	–	1.7
i-Butene	19.1	31.3	83.3	3.6
n-Butene	–	–	<0.1	2.3
i-Pentane	–	–	–	1.5
n-Pentane	–	–	–	0.6
Pentenes	–	–	–	2.5
C6+ Aliphatics	19.1	3.8	1.6	8.2
Benzene	–	–	–	2.6
Toluene	–	–	0.1	13.0
Ethylbenzene	–	–	–	2.7
Xylenes	–	1.3	2.1	22.3
1,2,3-Trimethylbenzene	–	<0.1	<0.1	1.1
1,2,4-Trimethylbenzene	–	7.0	2.0	8.8
1,3,5-Trimethylbenzene	59.3	52.5	2.6	0.6
Other C9 Aromatics	–	–	0.3	9.7

Gayubo et al. (2004a) also report the oligomerization of acetone on HZSM-5. Acetone and water (50% mol) were used in their experiment in a fixed-bed reactor with temperatures ranging from 250 to 450 °C with a temperature ramp of 0.5 °C/min. The space velocity was WHSV = 1.2 h^{-1} and the pressure was 1 atm (absolute). They studied the effect of temperature on the product distribution. Their results are more detailed than the results presented by Chang and Silvestri (1977). Profiles of aromatics, $C5^+$ olefins, $C4^+$ paraffins, ethenes, propenes, *n*-butenes, CO, CO_2, and water were recorded with changing temperature.

At low temperatures (250 to 300 °C), aromatic compounds are the most abundant. However, at higher temperatures the aromatic concentration decreases and the concentration of $C5^+$ olefins and isobutene increases.

Gayubo et al. (2004a) showed the effect of co-feeding the acetone/water mixtures with nitrogen, which inhibited the production of aromatics and $C4^+$ paraffins. Nitrogen increased the selectivity of propene and $C5^+$ olefins. Also, nitrogen reduced catalyst deactivation because it attenuates coke formation.

Silvestri et al. (1989) explained the mechanism of acetone condensation (see Figure 2.6). Over an acid catalyst, the first reaction product of acetone is diacetone alcohol. Then, this ketone alcohol is transformed to mesityl oxide ($CH_3C(O)CH=C(CH_3)_2$) and water. Then the mesityl oxide reacts with acetone forming most of the reaction products of the condensation of acetone, e.g., phorone, isophorone, isobutene, acetic acid, mesytilene, and others.

Figure 2.7 (Salvapati et al. 1989) shows the transformation of mesytil oxide to acetic acid and isobutene. This reaction is important because isobutene is oligomerized to mesitylene. According to Silvestri et al. (1989), all the aromatic compounds are formed from mesytilene. The cracking reaction of mesytilene produces xylenes, toluene, and benzene, in that order. Figure 2.8 shows the aromatization reaction path of the cracking of mesitylene.

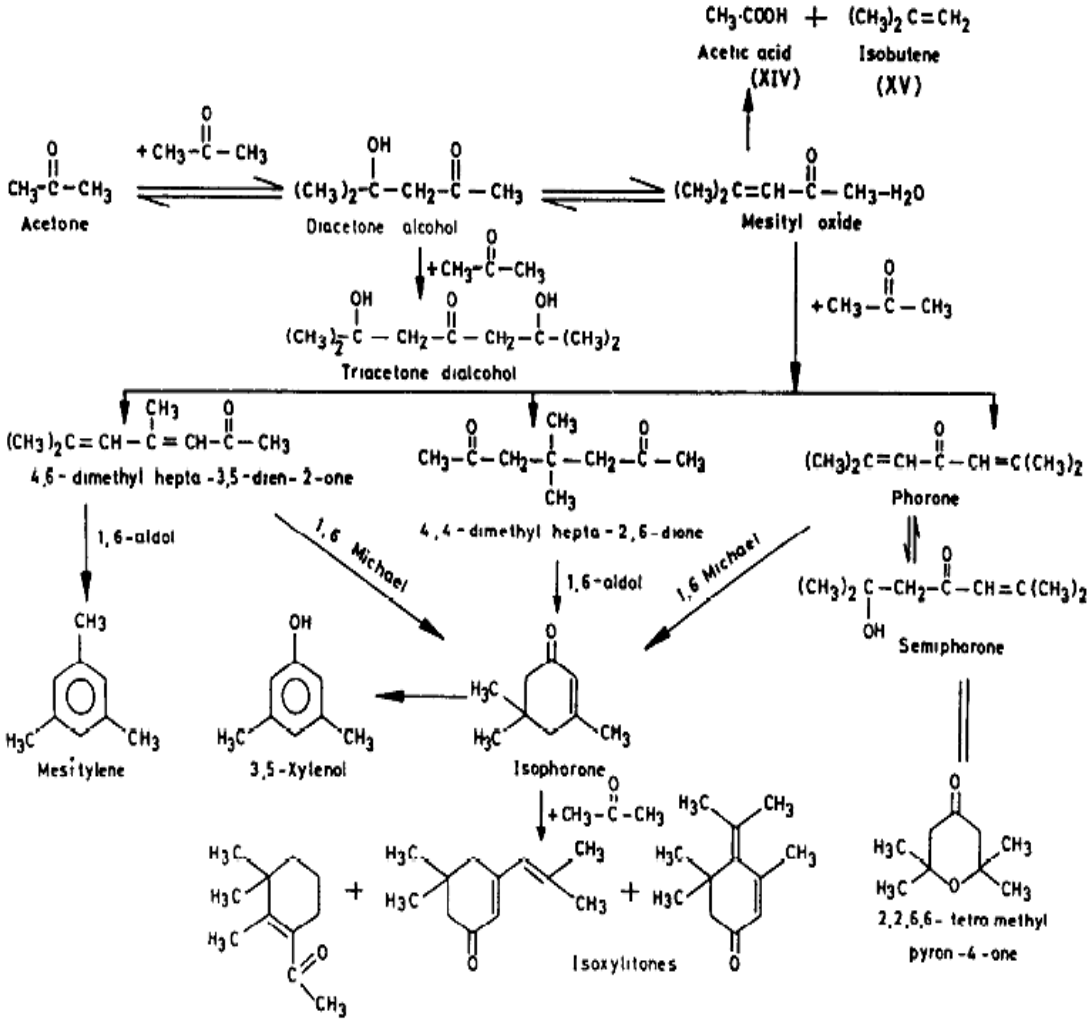

Figure 2.7. Formation of reaction products in the autocondensation of acetone (Salvapati et al. 1989).

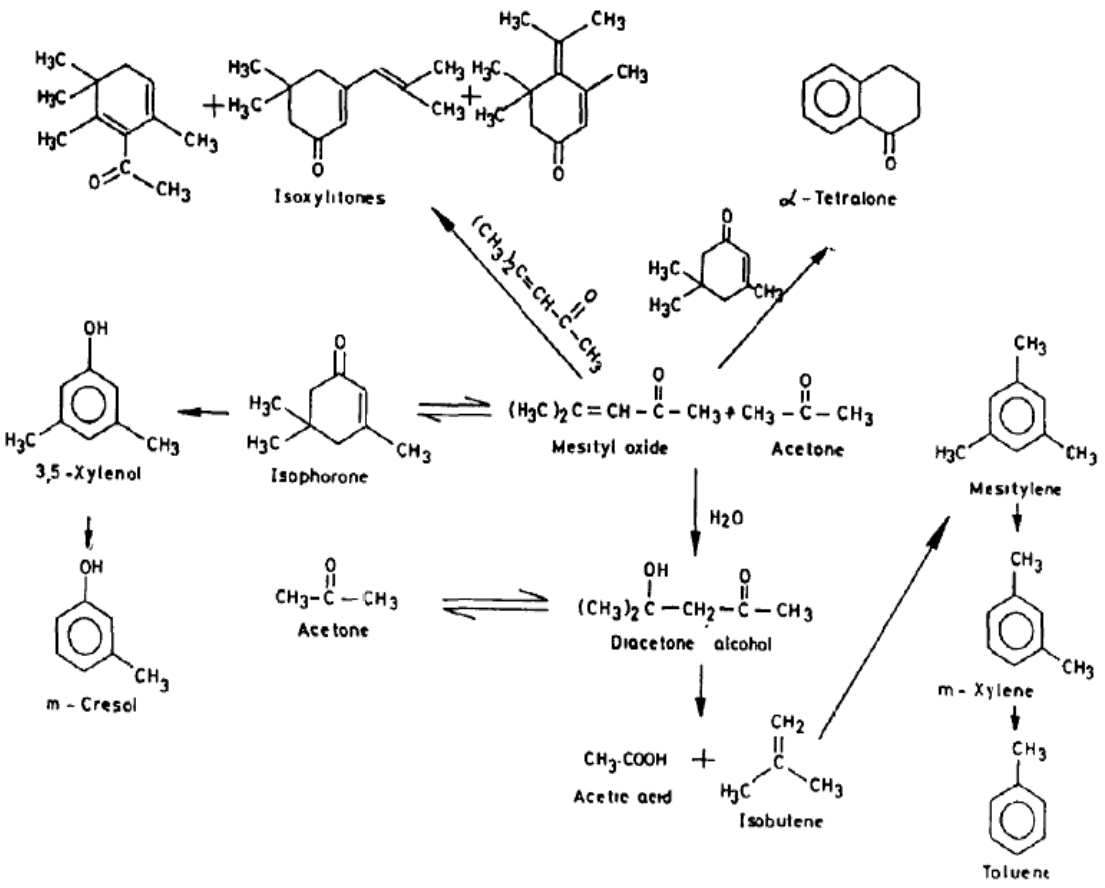

Figure 2.8. Reaction paths in the aromatization of isophorone (Salvapati et al. 1989).

CHAPTER III

EXPERIMENTAL PROCEDURE AND EQUIPMENT

3.1 Experimental Apparatus

A packed-bed reactor was used in these experiments (Figure 3.1). The apparatus has two major components: gas chromatograph and reactor.

The reactor unit consists of a packed-bed reactor, a pre-heater, a syringe pump, mass flow meters, and gas lines for hydrogen, nitrogen, and air. The reactor and the pipes are constructed of 316-type stainless steel.

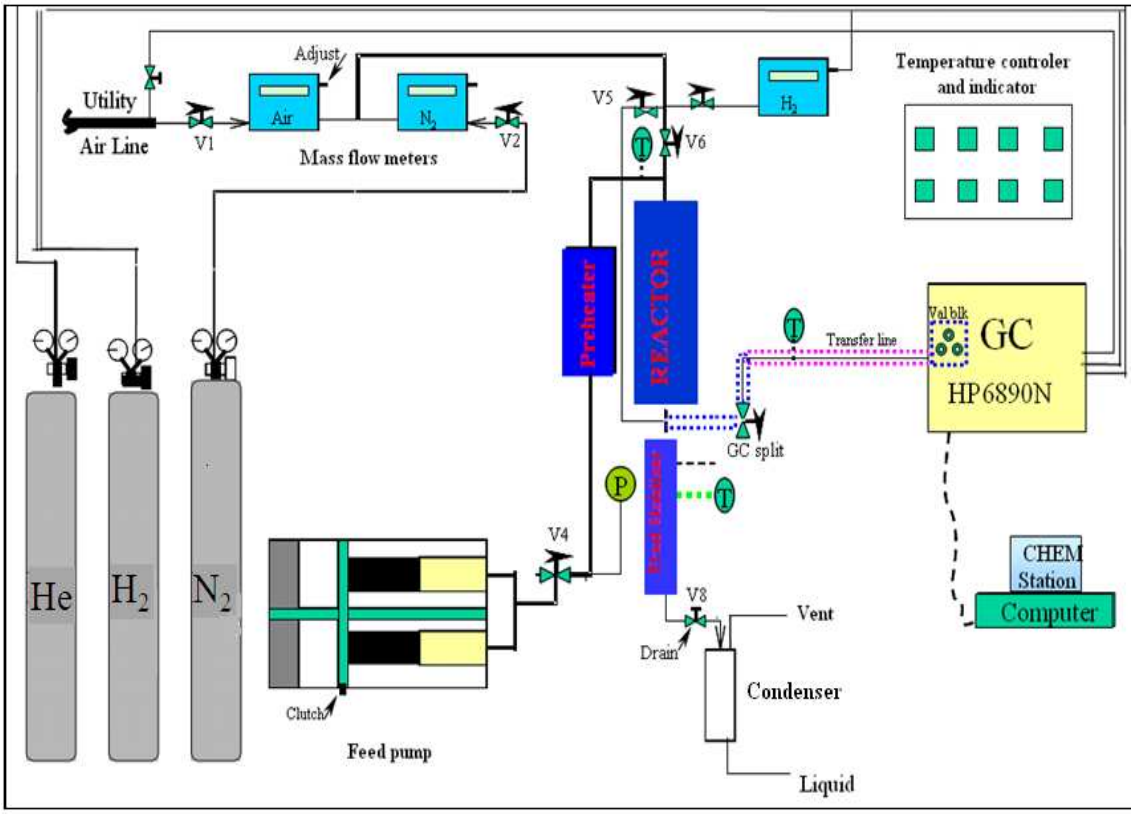

Figure 3.1. Schematic diagram of the apparatus.

The pump injects liquid into the preheater to gasify it. The preheater temperature is around 420 °C. Then, after the liquid becomes gas, it goes through a reactor where it contacts the HZSM-5 catalyst and reacts. Later, the reaction products go through a stabilizer where the temperature is around 200 °C. This stabilizer ensures that all the products are in the gas phase for the gas chromatograph. Finally, an ice-cooled condenser separates liquid from gas. The gas goes to a vent whereas the liquid is collected for a gas chromatograph-mass spectrograph analysis.

The gas chromatograph (Agilent Technology Model 6890N) has two detectors (TCD and FID) to analyze reaction products. The GC has six 30-m mega-bore capillary columns: a methyl silicone HP-1, two HP Plot Q, HP Mole Sieve, a HP Plot Alumna and a 5% phenyl methyl silicone HP-5. All columns have about 40- to 50-µm-thick phases. The GC has three valves that split the sample into the six columns. These six columns better separate the samples and consequently give more accurate results.

Figure 3.1 shows a schematic of the catalyst bed, which has catalyst in the middle section and α-alumina on the top and bottom as filling material. Table 3.1 indicates the properties of HZSM-5 catalysts used in the experiments. Table 3.2 shows more information about the reactor dimensions.

Three HZSM-5 catalysts were used in these experiments: (1) a proprietary catalyst from 280, (2) commercial HZSM-5 (80), (3) and commercial HZSM-5 (280). The three types of catalysts have similar physical properties (see Table 3.2). The isopropanol reactor used 4.2 g whereas the acetone reactor used 6.0 g. The procedure followed for the acetone and isopropanol reaction is in Appendix F.

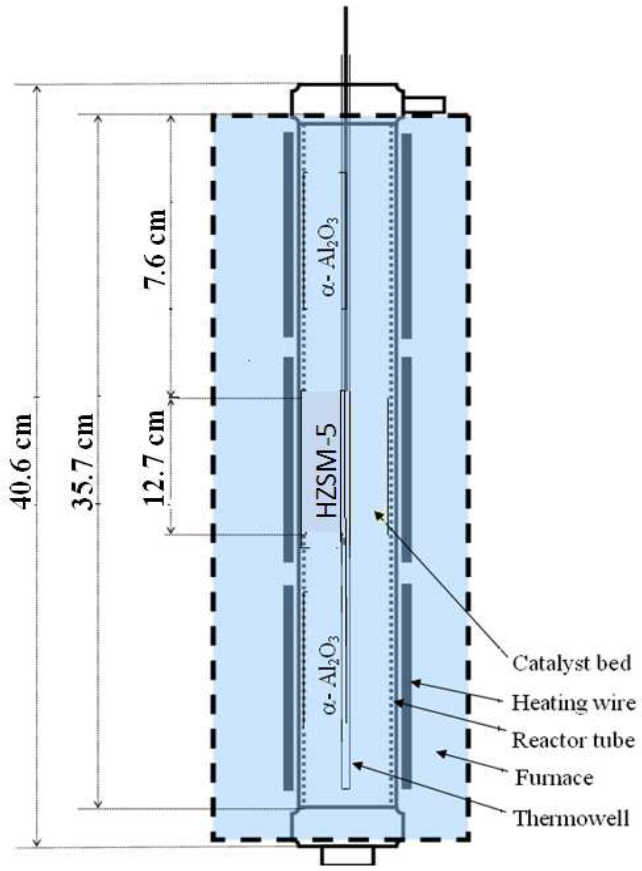

Figure 3.2. Schematic diagram of the reactor bed.

Table 3.1 Catalyst physical properties.

Properties	Values
Si/Al ratio (mol silica/ mol alumina)	80, 280, and 280
Shape	Cylinder
Particle height (mm)	3.5 (average)
Particle diameter (mm)	1.6
Particle bulk density (kg/m^3)	750
Particle density (kg/m^3)	1800
Void fraction of packed bed ε_0	0.58
Surface area (m^2/g)	425, 400

Table 3.2 Reactor dimensions.

Properties	Values
Internal diameter (cm)	1.0
External diameter (cm)	1.3
Thermowell diameter (cm)	0.14

3.2 Product Analysis

To analyze the products, it was necessary to have two chromatographs:

- Gas chromatograph (Agilent Technology Model 6890N)
- Gas chromatograph-mass spectrograph (HP Model G1800C)

The gas chromatograph (GC) is connected on-line with the reactor. This GC has a flame ionization detector (FID) and a thermal conductivity detector (TCD). The TCD analyzes light hydrocarbon products (C1–C4), CO, CO_2, and water. The FID is used for the heavier hydrocarbons (C5–C13). All the reaction products were analyzed with this chromatograph; however, heavier hydrocarbons (C5–C13) were lumped by carbon number. To know all the isomers in the liquid phase, it was necessary to perform a more detailed analysis of the sample with a GC-MS.

The gas chromatograph-mass spectrograph (GC-MS) analyzes the liquid product samples. Before the analysis, all reaction products were cooled to 15°C to ensure that all hydrocarbons with more than five carbons in their molecule were in the liquid phase. A GC-MS analysis of the liquid phase typically determines that the liquid samples have over 100 compounds. The compounds were described by carbon number and types of products (i.e., paraffins, oxygenated compounds, olefins, naphtenes, naphtenes olefinics, and aromatics). The carbon number ranges from C4 to C14. Table 3.3 shows an example of how the compound analysis was reported.

Table 3.3 Liquid product analysis from GC-MS data.

C#	Paraffins	Oxy	Olefins	Isoparaffins	Naphtenes	Naphtenes Olefinics	Aromatics	Total
4	–	–	–	–	–	–	–	–
5	–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–
14	–	–	–	–	–	–	–	–
Total	–	–	–	–	–	–	–	100

For isopropanol and acetone, the concentration of the products is recorded. Due to the differences in the mechanism of the reaction between isopropanol and acetone, the experiment collection of data was different. In chapter 4 and 5 from this thesis, the plan for each experiment is explained; however, the overall objective is to measure the effect of the reaction conditions change in the reaction product concentration.

CHAPTER IV

RESULTS AND DISCUSSION OF ISOPROPANOL REACTION OVER HZSM-5

For the isopropanol reaction, the product has liquid and gaseous phases. For the liquid product, the water is decanted and the liquid hydrocarbon is separated. All the products are detected by the on-line GC (C1-C13); however the liquid ($C5^{+}$) is collected to analyze it in a GC-MS and identify the isomers.

4.1 Definitions

The isopropanol feed rate is characterized by the weight hourly space velocity (WHSV). The weight hourly space velocity (WHSV) is defined as the weight of feed per hour per unit weight of catalyst loaded in the reactor. For example, if the feed rate is 10 g per hour to the reactor and 10 g of catalyst loaded in the reactor, the WHSV is 1.0 h^{-1}.

$$\text{WHSV} \equiv \frac{\dot{m}_{feed}}{m_{catalyst}}$$

where

$\dot{m}_{feedstock-fed}$ = mass flow rate to the reactor (g/h)
$m_{catalyst}$ = mass of catalyst (g)

Conversion is the percentage of reactants converted to products. For example, 100% conversion means all the reactants converted to products.

$$\text{Conversion (\%)} \equiv \frac{\dot{m}_{feedstock-reacted}}{\dot{m}_{feedstock-fed}} \times 100$$

where

$\dot{m}_{feedstock-reacted}$ = rate of reaction (g/h)

$\dot{m}_{feedstock-fed}$ = mass feed rate to the reactor in one hour (g/h)

Concentration is the measure of how much of a given substance there is mixed with another substance.

$$\text{Concentration (wt\%)} \equiv \frac{m_i}{m_T}$$

where

m_i = mass flow rate of the product Component *i* (g)

m_T = total mass of the products (g)

This last term can be of two types: 100 g C all product (Figure 4.1) or 100 g C liquid hydrocarbon product (Figures 4.4 and 4.5). Water is not considered in the total product. For all the experiments the concentration is referred on a carbon basis.

Calculations:

The product is in both the gas and liquid phases. The gaseous products are hydrocarbons with less than five carbons in their molecule (e.g., methane, ethane, ethene, propene, propane, butane, isobutene, butane, isobutylene), carbon monoxide, and carbon dioxide. The liquid products are hydrocarbons with five or more carbons in their molecule (e.g., pentanes, benzene, naphthalene). For each experiment, six samples were taken.

For the isopropanol reaction, nine experiments were performed with temperatures ranging from 300 to 410 °C. The weight hourly space velocities (WHSV) studied were 0.52, 1.32, 1.87, 3.74, 7.94, and 11.23 h^{-1}. The pressure was 1 atm (absolute). All the experiments for the isopropanol reaction were over HZSM-5 (280). The conversion for all these experiments was 100%. Table 4.1 shows all the experiments for the isopropanol reaction over HZSM-5 (280).

300 °C was chosen as initial temperature because lower temperatures were not stable during time which is because of the heat of reaction of isopropanol. For example, when the reaction was set between than 250 and 300 °C, the temperature always increased until it reached 300 °C. On the other hand if the temperature was lower than 250 °C, the isopropanol did not react.

The WHSV ranged between 0.52 and 11.23 h^{-1}. The WHSV 0.52 h^{-1} was chosen because of the size of the reactor and pipes. Lower WHSV would not have obtained a constant flow on the exit of the reactor. WHSV more than 11.23 h^{-1} presented problems controlling a constant temperature along the catalyst bed (it is necessary to have the same temperature along the catalyst bed).

For each condition, two experiments of six-hour reactions were preformed. Each experiment had 5 measurements on average during time. This means that for each condition, there were around 10 measurements. The catalyst was always regenerated before each experiment. The GC collected and measured the results for each condition. Figure 4.1 shows the results for two experiments of isopropanol reaction at the same conditions; the conditions were catalyst = HZSM-5 (280), T = 410°C, WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

The reaction of isopropanol over HZSM-5 is exothermic. The temperature raised about 40 °C from the set temperature. The isopropanol decomposes to water and hydrocarbons.

$$C_3H_8O \rightarrow 3[CH_2] + H_2O$$

where $[CH_2]$ represents olefins, paraffins, naphtenes, and aromatics. The product distribution was from compounds with two carbons (e.g., ethane) to molecules with 13 carbons (e.g., naphthalene).

The liquid has two phases: oil and water. The oil liquid phase contains heavy hydrocarbons (e.g., pentanes, cyclohexanes, xylenes, heptanes, and branched aromatics). For all cases, no CO_2 or CO was formed. All the oxygen in the isopropanol molecule formed water. For example, if 60 grams of isopropanol reacted, 18 grams of water were produced. At 1 atm (absolute), the effect of temperature and WHSV are studied for isopropanol reaction over HZSM-5 (280).

Table 4.1 Experiments for the isopropanol reaction over HZSM-5 (280).

	Catalyst: HZSM-5 (280)					
	WHSV (h^{-1})					
T (°C)	0.5	1.3	1.9	3.7	7.9	11.2
300		I1				
320		I2				
370	I5	I3	I6	I7	I8	I9
410		I4				

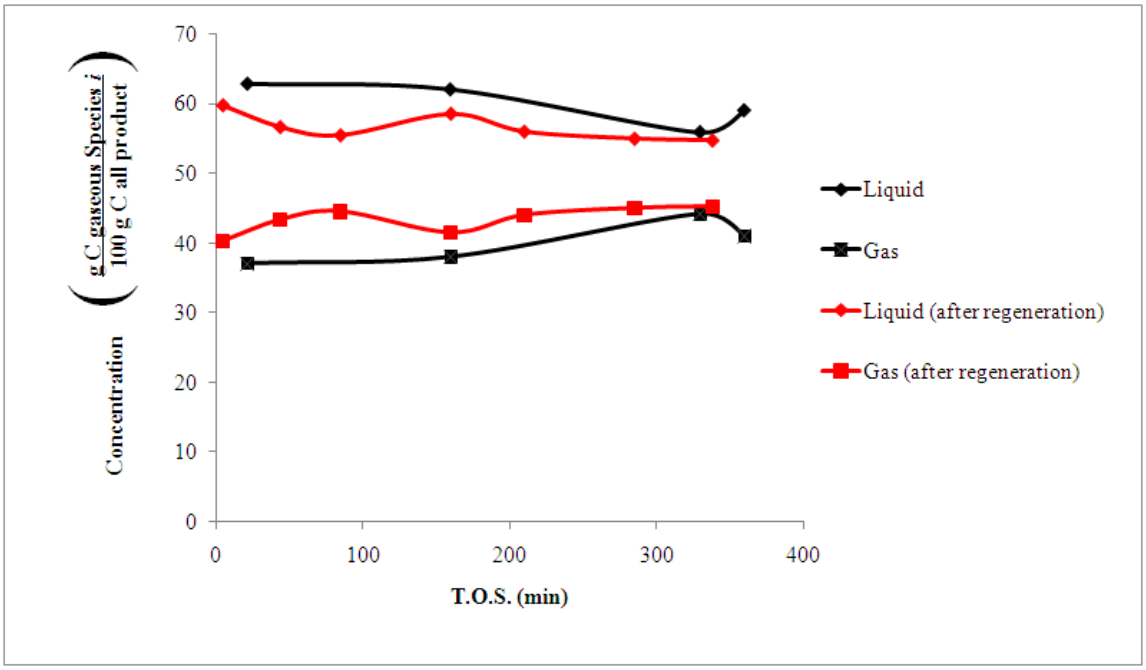

Figure 4.1 Product distribution of gases and liquids for the isopropanol reaction over HZSM-5 (280), T = 370 °C, WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

Figure 4.1 shows gas and liquid product distribution for the isopropanol reaction over HZSM-5 over time on stream, and it illustrates that the product distribution does not change during time for the two experiments. The black lines show the product distribution of liquid and gas with fresh catalyst, and the red lines the product distribution after regeneration. For the fresh and regenerated catalyst, it is noteworthy that the concentration of liquid and gas are the same and relatively constant during time. For all the experiment of temperature and WHSV, the concentration value shown was an average of all the values recorded in 6 hours.

4.2 Effect of Temperature

Four experiments at different temperatures were performed, as summarized in Table 4.2 with a WHSV = 1.31 h^{-1}. Figure 4.2 shows the gas and liquid product distribution for the isopropanol reaction over HZSM-5. The gas phase has hydrocarbons from C1 to C4 and, the liquid phase has hydrocarbons from C5 to C13 (WHSV = 1.31 h^{-1}, P = 1 atm (absolute)). The product concentration was always constant during the first 6 h; therefore, the catalyst showed no deactivation during this time. Temperature affects the selectivity of gas and liquid products. The amount of liquid $C5^{+}$ decreased from 70% (300°C) to 40% (410°C), as temperature increased. The gaseous products increased from 30% (300°C) to 60% (410°C).

Table 4.2. Experiments showing the effect of temperature for isopropanol reaction over HZSM-5 (280).

	Catalyst: HZSM-5 (280)					
	WHSV (h^{-1})					
T (°C)	0.5	1.3	1.9	3.7	7.9	11.2
300		I1				
320		I2				
370		I3				
410		I4				

Figure 4.3 and Table 4.3 show the gas product distribution of the isopropanol reaction at different temperatures. Isobutene and butane are the most abundant reaction products. The concentration of gaseous products, such as 2-butene and isobutylene, increases at high temperature. According to Gayubo et al. (2004b), the increase of gaseous products results from $C5^{+}$ olefins and aromatics at high temperatures. For instance, in Figure 4.3, the amount of propane increases from 2% (300 °C) to 13% (410 °C). It is notable that the amount of olefinic gaseous products is larger than the amount of paraffinic products. Figure 4.4 shows the water yield. The water yield increases with temperature because the amount of liquid hydrocarbons decreases.

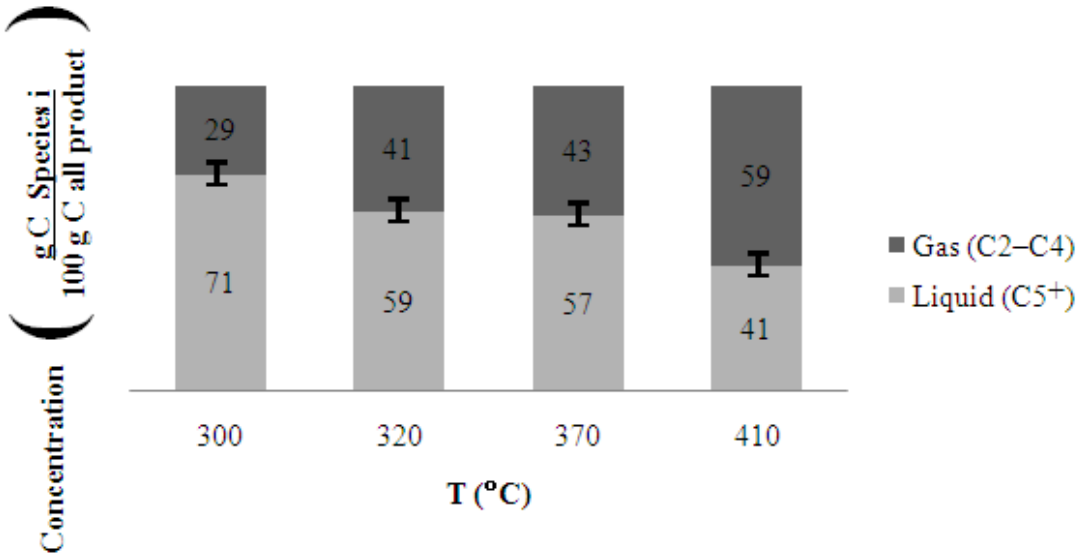

Figure 4.2. Product distribution of gases and liquids for the isopropanol reaction over HZSM-5 (280), WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

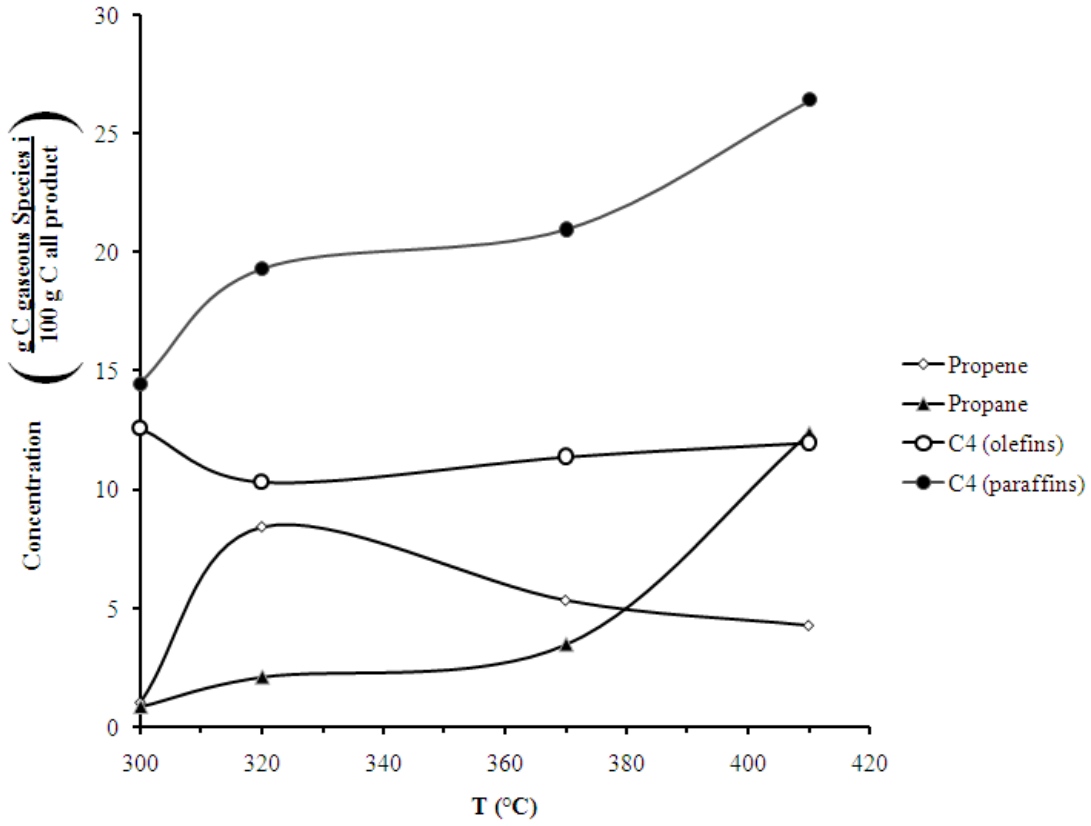

Figure 4.3 Product distribution of gases for the isopropanol reaction over HZSM-5 (280), WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

Table 4.3 Gaseous products for the isopropanol reaction over HZSM-5 at different temperatures, WHSV= 1.31 h^{-1}, *P* = 1 atm

	Concentration (g C gaseous Species *i* /100 g C all product)			
	Temperature (°C)			
	300	320	370	410
Ethene	0.3	1.1	1.6	3.2
Propene	1.1	8.4	5.3	4.3
Propane	0.9	2.1	3.5	12.4
Isobutane	0.5	9.4	9.0	22.1
Butane	14.0	9.9	12.0	4.3
Isobutylene	8.0	7.7	8.1	10.7
2–butene	4.7	2.6	3.3	1.3

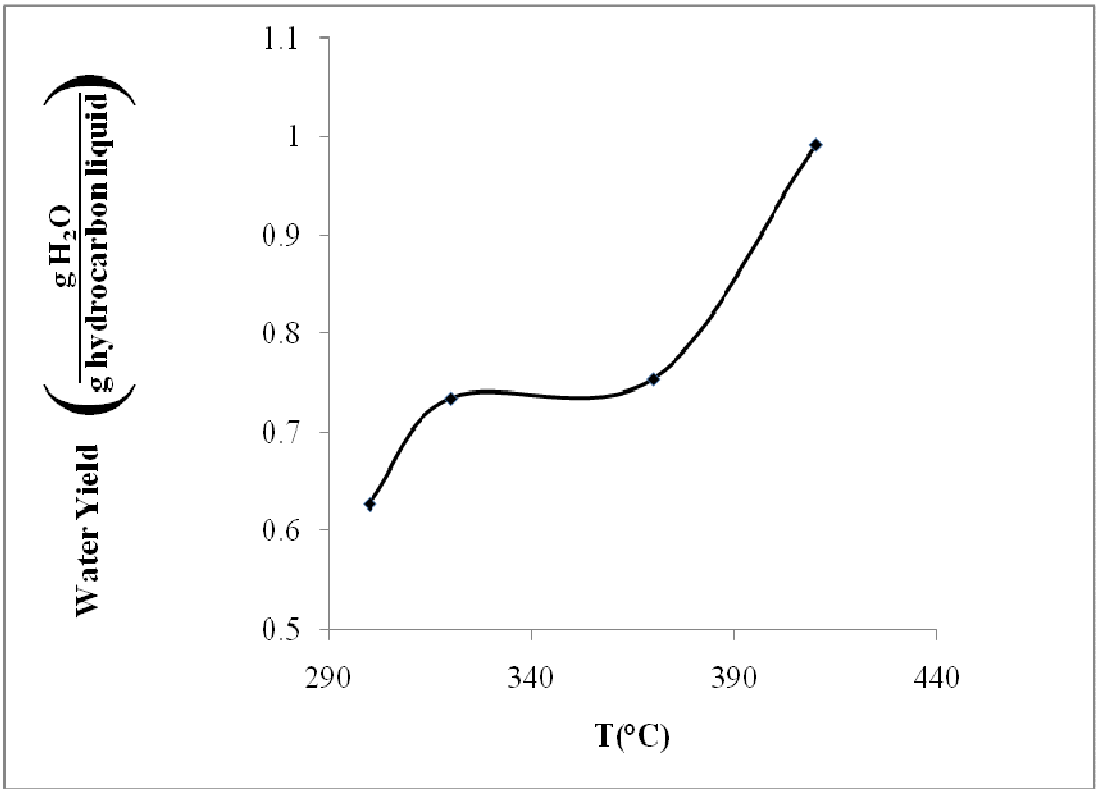

Figure 4.4. Water yield for the isopropanol reaction over HZSM-5(280), WHSV = 1.31 h^{-1}, *P* = 1 atm (absolute).

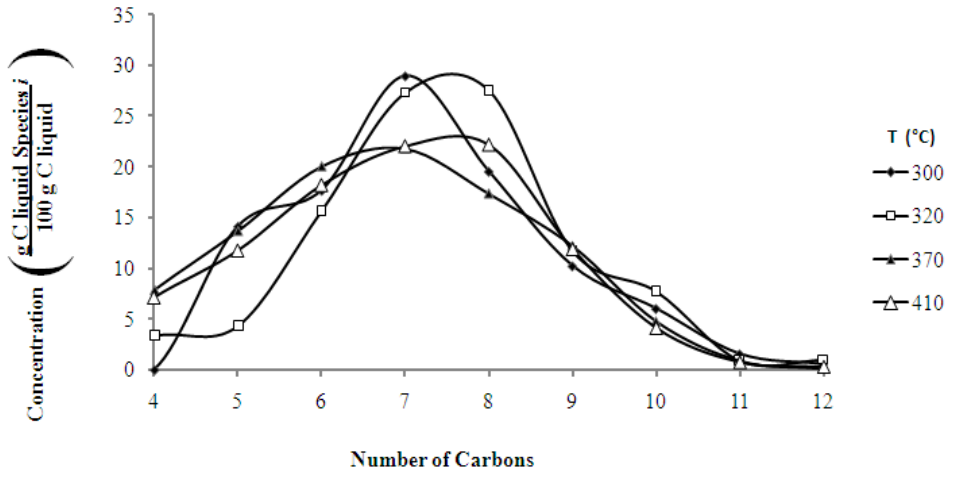

Figure 4.5. Carbon liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

Figure 4.5 illustrates the carbon distribution of liquid products at different temperatures. The concentration shown in Figure 4.5 represents the oil liquid phase. At all temperatures, the most abundant components in the oil phase are C7 and C8. The curves tend to be sharper at low temperatures and wider at high temperatures. At higher temperatures, the amount of C4 dissolved in the oil phase increases because the concentration of C4 increases with temperature (Figure 4.2) and it is absorbed by the oil phase.

Temperature affects the type of liquid reaction products obtained (Figure 4.6). Olefins have the highest concentration (30 to 60%) in this temperature range. The concentration of aromatic and naphtenes olefinics increases from 5% (300°C) to more than 20% (410°C). The concentration of isoparaffins and naphtenes are constant at all temperatures. The concentration of isoparaffinic compounds is always below 10%. The paraffin concentration is negligible.

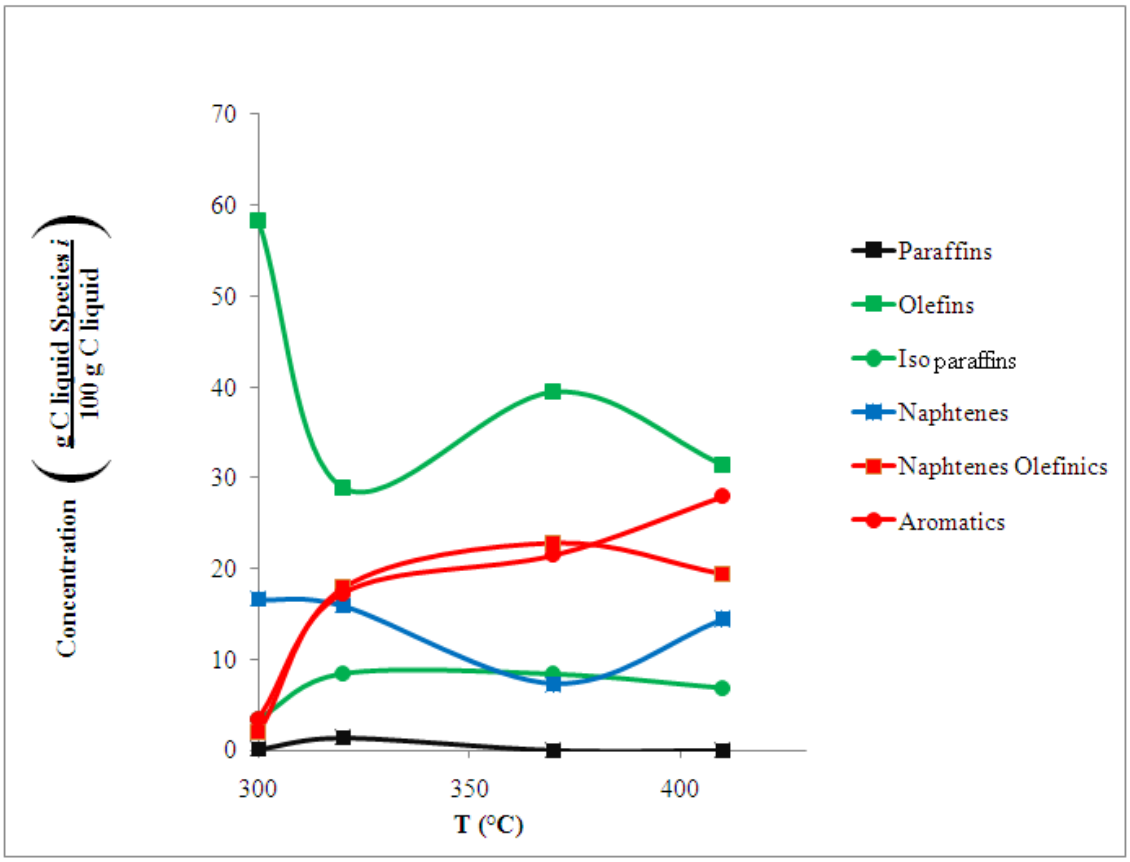

Figure 4.6. Liquid type product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.31 h^{-1}, *P* = 1 atm (absolute).

Table 4.4 shows the concentration range of the most abundant components found in the oil phase for this set of experiments. As expected from Figure 4.6 and Table 4.4, the most abundant compounds are olefinics. It is of note that the most abundant compound depends on the carbon number. For example, olefinics compounds are more abundant from C4 to C6, naphtenes from C6 to C8, and aromatics from C8 to C10 (Figure 4.7).

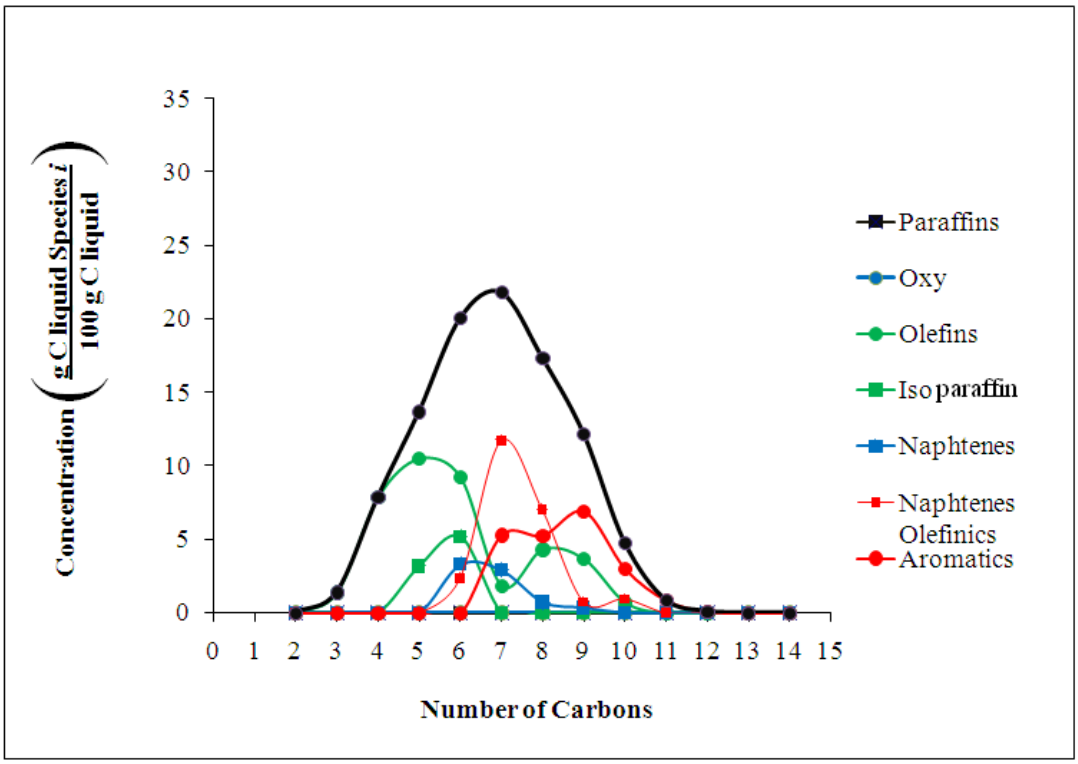

Figure 4.7. Liquid type product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.31 h^{-1}, P = 1 atm (absolute), T = 370 °C.

Table 4.4 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), T = 300–415°C, WHSV = 1.31 h^{-1}, P = 1 atm (absolute).

Olefins and Naphtenes Olefinics (g C Species *i* /100 g C liquid)		Naphtenes (g C Species *i* /100 g C liquid)	
1-propene	1.4–1.5	cyclohexane	1.0–2.3
2-butene	3.3–7.7	methyl-cyclopentane	2.3–2.9
2-methyl-1-butene	4.7–5.3	cyclopentane, 1,2-dimethyl-3-methylene	1.7–1.9
		Aromatics (g C Species *i* /100 g C liquid)	
2-butene, 2,3-dimethy	1.6–6.6		
2-pentene, 2-methyl	2.6–4.2	toluene	1.6–3.4
2-pentene, 3-methyl	2.4–8.5	ethyl benzene	1.3–2.1
3-methyl-2-pentene	2.0–5.8	xylene	1.7–7.8
2-hexene, 2,3-dimethyl	1.9–5.1	mesitylene	1.8–2.6
1,5-dimethyl-cyclopentene	1.3–2.8		
1,3-dimethyl-cyclohexene	2.0–3.7		

4.3 Effect of the Weight Hourly Space Velocity (WHSV).

In this section, the effect of WHSV is investigated. Five experiments at different temperatures were performed. The effect of changing WHSV is investigated over HZSM-5 (280) catalyst. The conditions for this set of experiments are shown in Table 4.5. Figure 4.8 shows the product distribution of gas and liquid products at different WHSV (0.52, 1.87, 3.74, 7.49, 11.23 h^{-1}). The product distribution of gases and liquids is not affected by the change of WHSV. The amount of liquid is constant (60%) at all WHSV from 0.52 to 11.23 h^{-1}.

Figure 4.9 illustrates the gas product distribution at different WHSV. The most favorable component was butanes at all WHSV investigated. The amount of propene increases from 1% (0.52 h^{-1}) to 15.5% (11.2 h^{-1}). Table 4.6 shows the concentration variation of the most abundant gases at different WHSV. This may be explained that at high WHSV (low residence time), propene forms first and does not have time to continue reacting. Figure 4.10 shows that at different WHSV, the water yield is constant and ranges between 0.7 to 0.8 g H_2O/g liquid hydrocarbons.

Table 4.3 Experiments showing the effect of WHSV for isopropanol reaction over HZSM-5 (280).

	Catalyst: HZSM-5 (280)					
	WHSV (h^{-1})					
T (°C)	0.5	1.3	1.9	3.7	7.9	11.2
300						
320						
370	I5	I3	I6	I7	I8	I9
410						

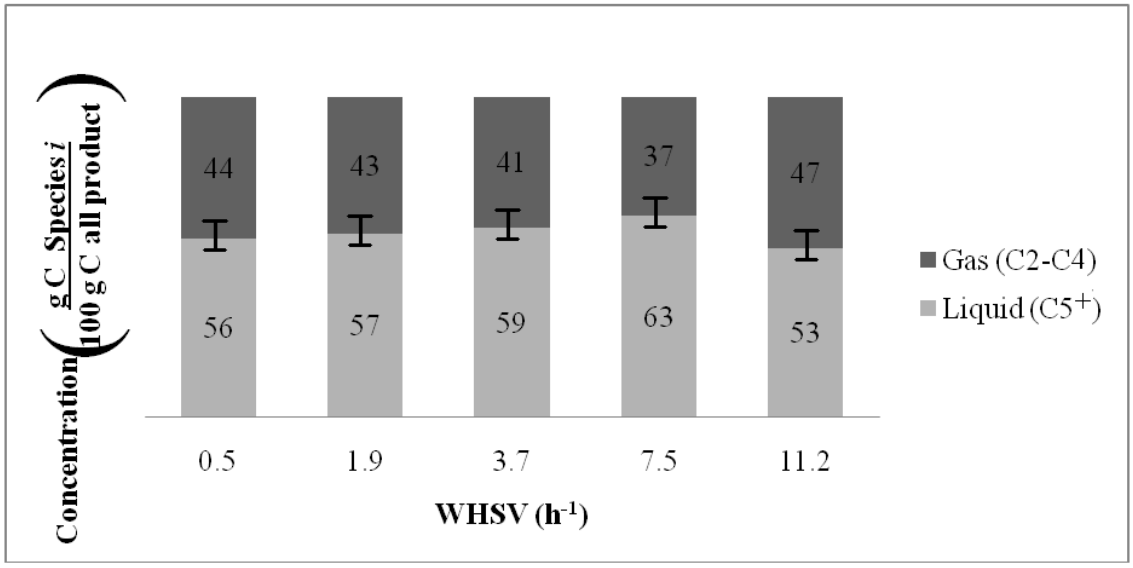

Figure 4.8. Product distribution of gases and liquids for the isopropanol reaction over HZSM-5 (280), T = 370 °C, P = 1 atm (absolute).

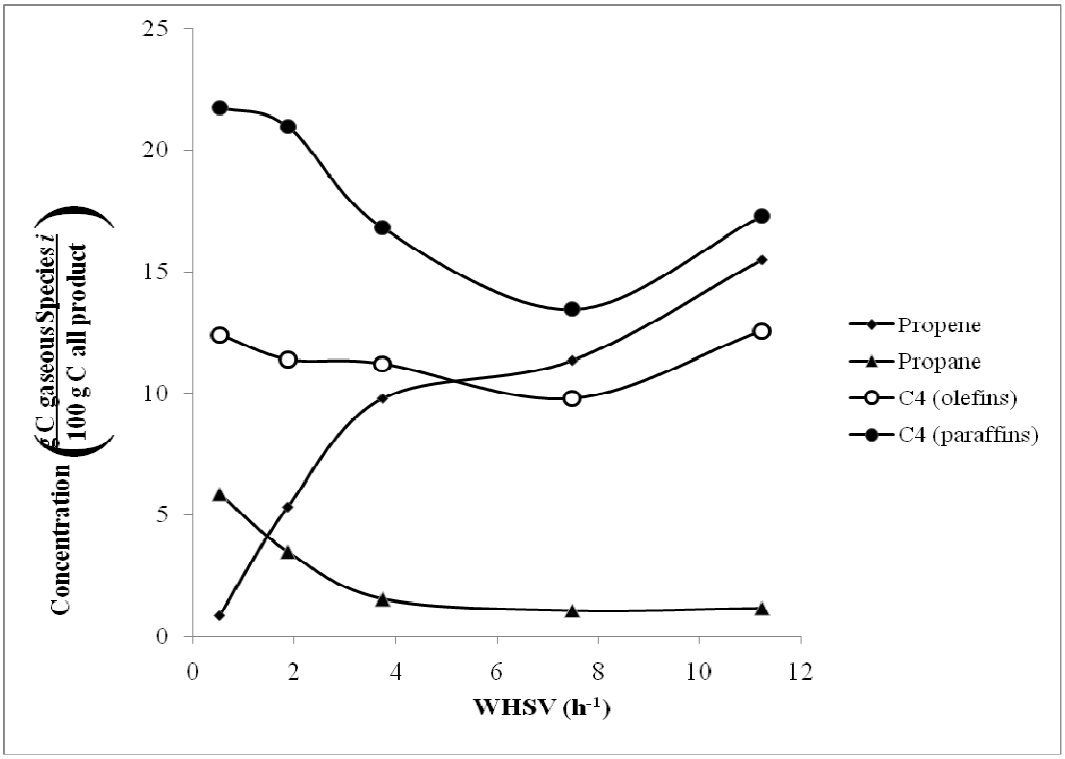

Figure 4.9. Product distribution of gases for the isopropanol reaction over HZSM-5 (280), T = 370°C, P = 1 atm (absolute).

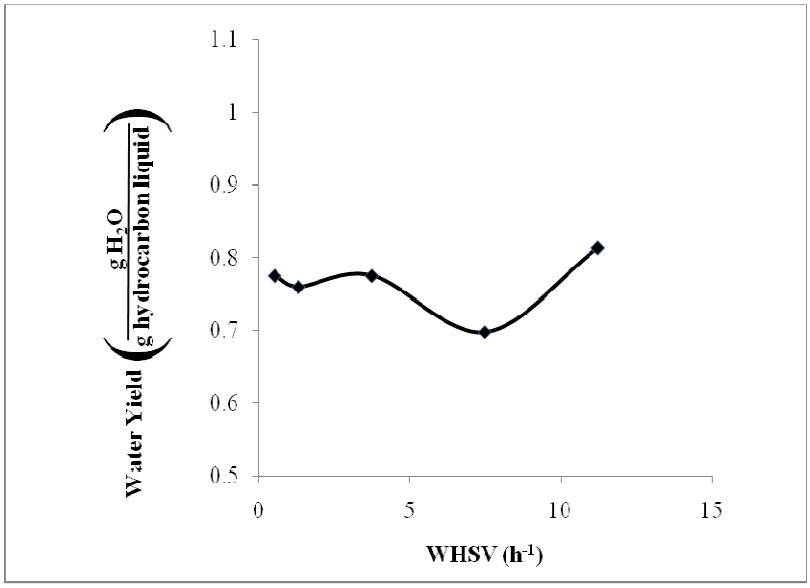

Figure 4.10. Water yield for the isopropanol reaction over HZSM-5 (280), T = 370°C, P = 1 atm (absolute).

Table 4.6 Gases products for the isopropanol reaction over HZSM-5 at different WHSV, T = 370 °C, P = 1 atm (absolute).

	Concentration (g C gaseous Species *i* /100 g C all product)				
	WHSV (h^{-1})				
	0.52	1.87	3.74	7.49	11.23
Ethene	3.0	1.6	1.4	1.2	0.7
Propene	0.9	5.3	9.8	11.4	15.5
Propane	5.9	3.5	1.6	1.1	1.2
Isobutane	11.0	9.0	3.5	1.7	2.2
Butane	10.8	12.0	13.4	11.8	15.1
Isobutylene	9.4	8.1	7.3	6.1	7.9
2-butene	3.0	3.3	3.9	3.7	4.7

Figure 4.11 illustrates the carbon distribution of the liquid products at different WHSV. WHSV significantly affects the carbon distribution of the liquid phase. At lower WHSV, the most abundant component is C9 whereas at higher WHSV, the most abundant component is C6. At low WHSV, the olefins can undergo more

oligomerization reactions to produce larger molecules, whereas at high WHSV, the molecules do not have time to form larger molecules. It is noteworthy that the carbon number in the liquid can only be changed by WHSV.

Figure 4.12 shows the reaction path that isopropanol reaction undergoes in these experiments.Figure 4.13 illustrates the type of products in the liquid phase at different WHSV. At very low WHSV, aromatics are high (60%); however, at high WHSV, the aromatics dropped drastically (8%). On the other hand, olefins go from 5% (0.52 h^{-1}) to 50% (11.2 h^{-1}). As well, naphtene olefinics increase from 7% (0.52 h^{-1}) to 30% (11.2 h^{-1}). The amount of paraffins always stayed below 5% in all samples. Table 4.7 shows ranges for the most abundant compounds in the liquid-phase product.

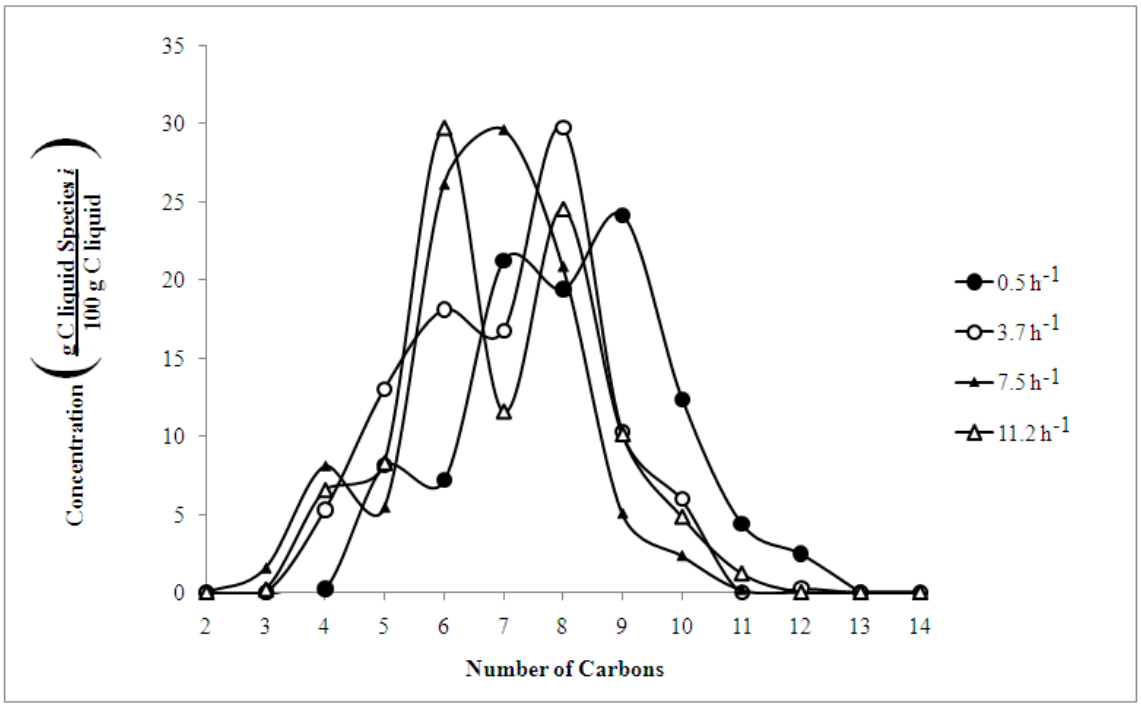

Figure 4.11. Carbon liquid product distribution of isopropanol reaction over HZSM-5 (280), *T* = 370°C, P = 1 atm (absolute).

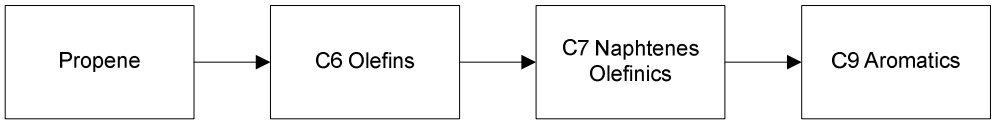

Figure 4.12. Reaction path of isopropanol.

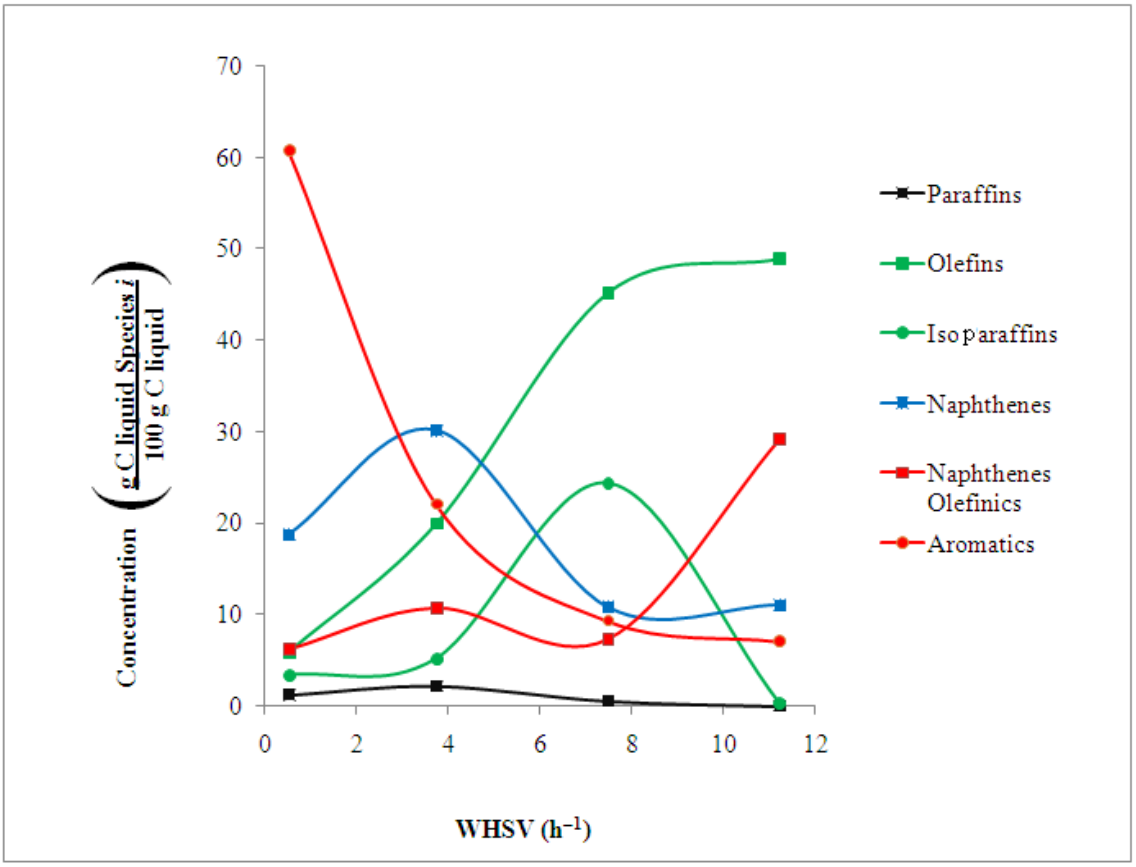

Figure 4.13 Liquid product distribution of isopropanol reaction over HZSM-5 (280), T = 370 °C, P = 1 atm (absolute).

In conclusion, the isopropanol reaction is very sensitive to temperature and WHSV. The distribution of products varies greatly with these two variables. The most abundant types of products from isopropanol are olefins, aromatics, naphtenes, and

isoparaffins. The gasoline obtained from isopropanol is slightly different from commercial gasoline (see Appendix A), which does not have olefins. However, the required carbon distribution of C8-centered can be met from the reaction products of isopropanol. The most similar product to commercial gasoline was obtained at T = 320 °C and WHSV = 1.3 h^{-1} at P = 1 atm (absolute).

The carbon distribution C8-centered (see Figure 4.14) and the low amount of gas were the criteria to choose the reaction conditions as optimal. At the conditions of T = 320 °C, WHSV = 1.3 h^{-1} and P = 1 atm (absolute), the gas concentration was less and the carbon liquid distribution was C8-centered.

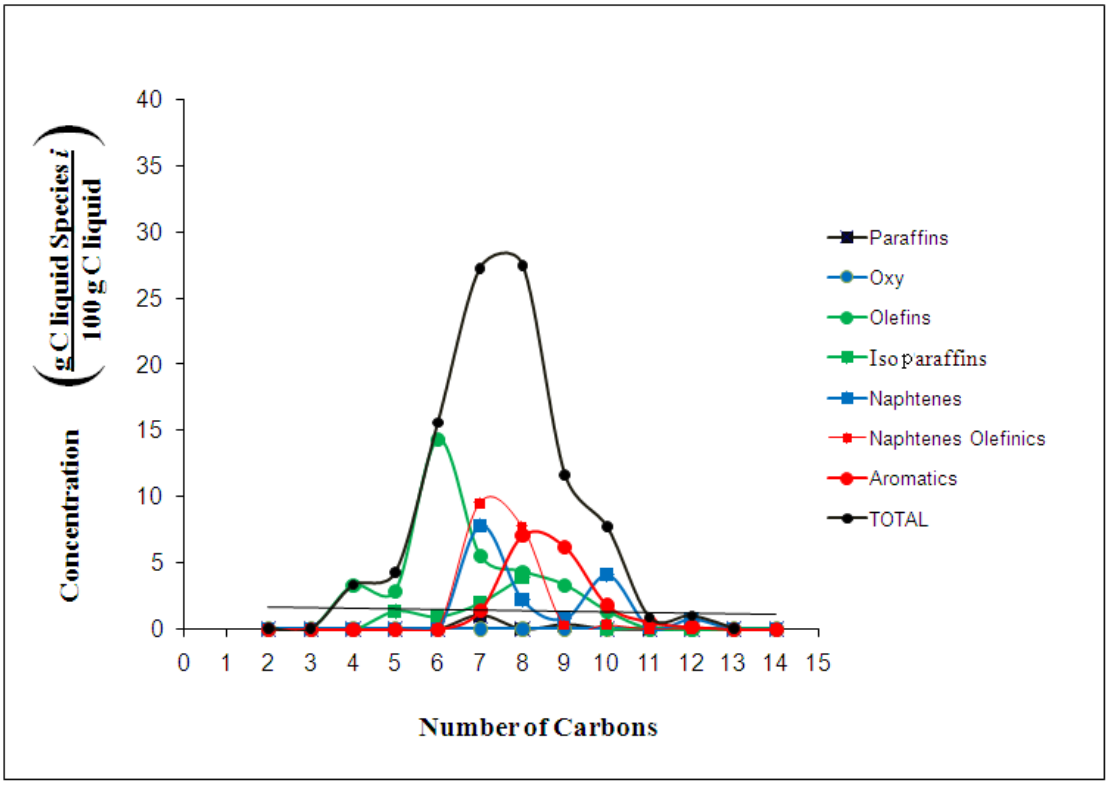

Figure 4.14. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 320°C.

Table 4.7 Most abundant compounds for the isopropanol reaction over HZSM-5, T = 370 °C, WHSV = 0.5–11 h^{-1}, P = 1 atm (absolute).

Olefins and Naphtenes Olefinics (g C Species *i* /100 g C liquid)		Naphtenes (g C Species *i* /100 g C liquid)		Aromatics (g C Species *i* /100 g C liquid)		Isoparaffins (g C Species *i* /100 g C liquid)	
1-propene	1.4–1.5	cyclopropane, 1,2-dimethyl	2.7–7.5	benzene, methyl	1.8–10	2-methyl pentane	4.2–4.4
1-butene, 2,3-dimethyl	5.5–6.6	cyclopropane, (1-methylethenyl)	1.4–2.7	benzene, 1,3-dimethyl	2.9–5.5	2-methyl,2-hexene	1.4–7.2
2,3-dimethyl-1-butene	2.4–6.8	cyclopentane, 1,3-dimethyl	1.8–2.7	benzene, 1-ethyl-2-methyl	2.2–4.4	2-methyl, hexane	2.4–2.8
2-pentene**,** 3-methyl	2.2–3.5	cyclopenatane, 1,2 -dimethyl-3-methylene	1.3–2.7				
3 methyl 2 pentene	3.7–9.5						
1,3-dimethyl-cyclohexene	2.0–2.9						
2-hexene, 2-methyl	1.2–7.8						
cyclohexene, 1,3-dimethyl	1.4–2.9						
cyclohexene, 1-methyl	1.8–2.3						

CHAPTER V

RESULTS AND DISCUSSION OF ACETONE REACTION OVER HZSM-5

Acetone reaction over HZSM-5 produces several products, such as hydrocarbons, oxygenated compounds, CO, CO_2, and water. Gaseous hydrocarbons include propene, butane, isobutene, and butene. Liquid hydrocarbons contain mainly of aromatics ranging from C6 to C14. The liquid products also include some oxygenated compounds, mainly isophorone (cyclohexanone, 3,3,5-trimethyl) and some phenols.

For the acetone reaction over HZSM-5, 34 experiments were performed. Temperatures ranged from 305 to 415 °C. The weight hourly space velocities (WHSV) studied were 1.32, 2.63, 3.95, 5.27, 6.58, 7.9 and 11.85 h^{-1}.The reaction pressures evaluated were 1 atm (absolute) and 7.8 atm (absolute). Table 5.1 summarizes experiments for the acetone reaction over HZSM-5 and the conditions for each experiment.

In addition, the effects of catalyst type, co-feeding hydrogen, pressure, and deactivation of catalyst were studied. The catalysts HZSM-5 used for the acetone reaction were commercial HZSM-5. Two types of catalyst used, with silica to alumina ratios of 80 and 280 mol silica/mol alumina, described as HZSM-5 (80) and HZSM-5 (280), respectively.

For the acetone reaction, the desired product is a mixture of hydrocarbons similar to commercial gasoline. The objective is to find the best reaction conditions to produce this synthetic gasoline. Several commercial gasolines from different gas station are in Appendix A and they will help as a referent to compare the reaction product.

Table 5.1 Experiments for the acetone reaction over HZSM-5.

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	A1						
		350		A2	A3	A4	A5			
		415		A6	A7	A8	A9	A10	A11	
			0.3	A12	A13	A14				
			0.5	A15	A16	A17				
	280		0	A18	A19	A20	A21	A22		
			03	A23						
			0.5	A24	A25					
			1	A27	A28					
7.8	280		0	A30		A31	A32		A33	A34

5.1 Catalyst Deactivation

For the acetone reaction, the catalyst deactivated because the concentration of products were not constant during the time on stream. The data for four experiments are presented to study catalyst deactivation (see Table 5.2). In these experiments, the product concentration was measured during time on stream.

Table 5.2 Catalyst deactivation experiments for the acetone reaction over HZSM-5.

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0							
		350								
		415		A6						
			0.3							
			0.5							
	280		0	A18						
			0.3	A23						
			0.5							
			1							
7.8	280		0	A30						

Figure 5.1 shows the percentage of liquid and gas with respect to time on stream (T.O.S) for acetone over HZSM-5 (80) at T = 410 °C and WHSV = 1.3 h^{-1} and P = 1 atm (absolute). The conversion was 100% at all times.

The gas phase contains hydrocarbons from C1 to C4, CO_2, and CO, and the liquid phase contains hydrocarbon $C5^+$ (mainly aromatics). Figure 5.1 shows that with time, the yield for gaseous products decreases and the yield for liquid products increases. Therefore, the product selectivity changes with time, which is attributed to catalyst deactivation.

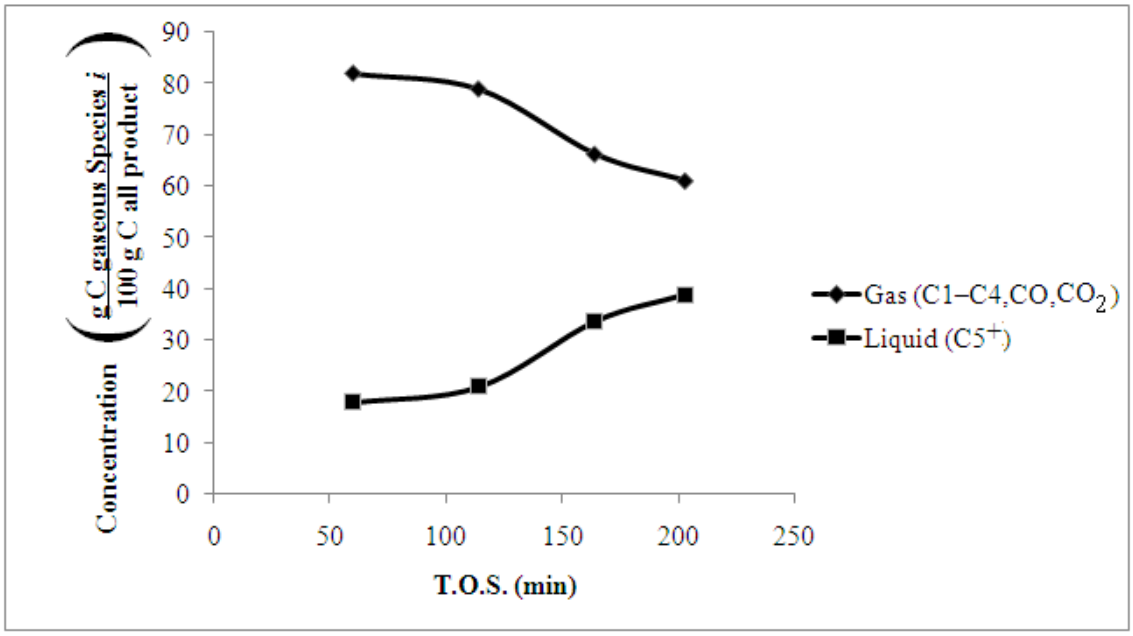

Figure 5.1. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.2 shows the product distribution of the gas phase with respect to time on stream (T.O.S) for acetone over HZSM-5 (80) at T = 415 °C and P = 1 atm (absolute) and WHSV = 1.3 h^{-1}. Only gases with concentrations over 5 wt% are reported. The most abundant gases are propane and isobutane. The tendency for all the gaseous products is to decrease with time.

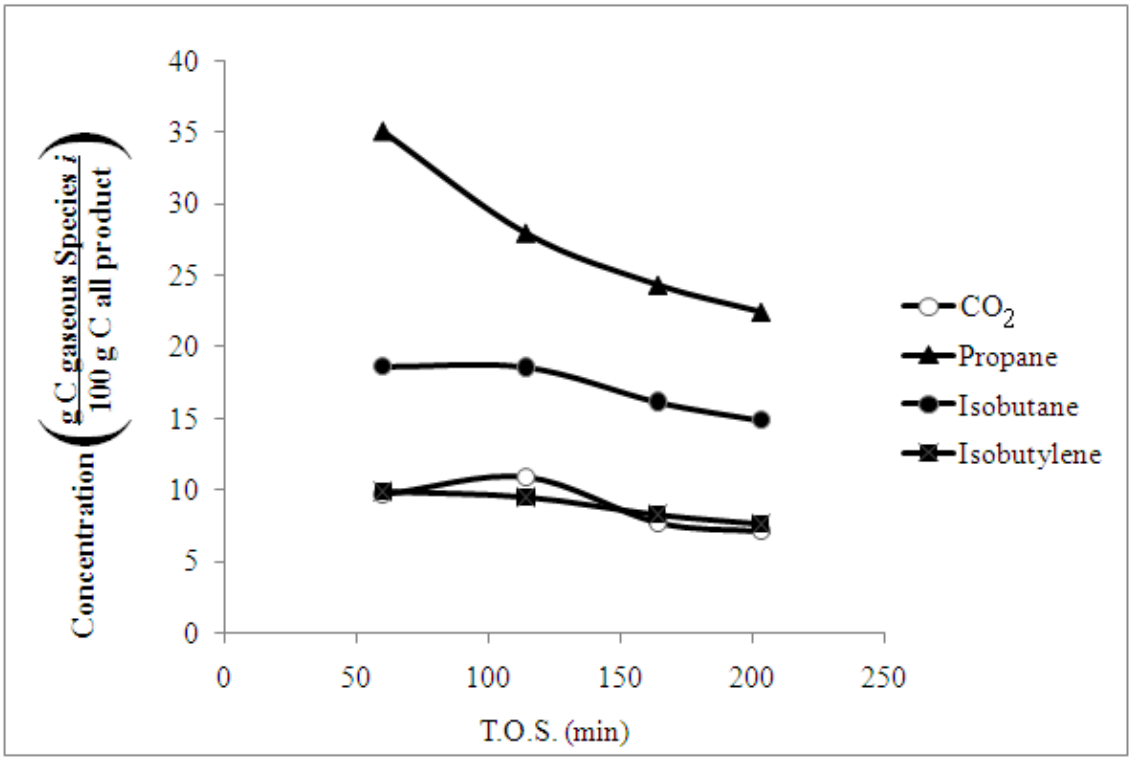

Figure 5.2. Product distribution of gases for the acetone reaction over HZSM-5 (80), T = 415 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.3 shows the product distribution of liquid and gas phases with respect to time on stream (T.O.S) for acetone over HZSM-5 (280) for T = 415 °C and WHSV = 1.3 h^{-1}. The yields for gaseous products and liquid hydrocarbons did not change during the first 150 min; thus, the deactivation of HZSM-5 (280) is lower than HZSM-5 (80). HZSM-5 (280) is less acidic and is slow to deactivate compared to HZSM-5 (80). For this set of experiments, the conversion is 100%. It is noteworthy that HZSM-5 (280) produces 10% of gases, which is much less than the 40% of gases produced with HZSM-5 (80).

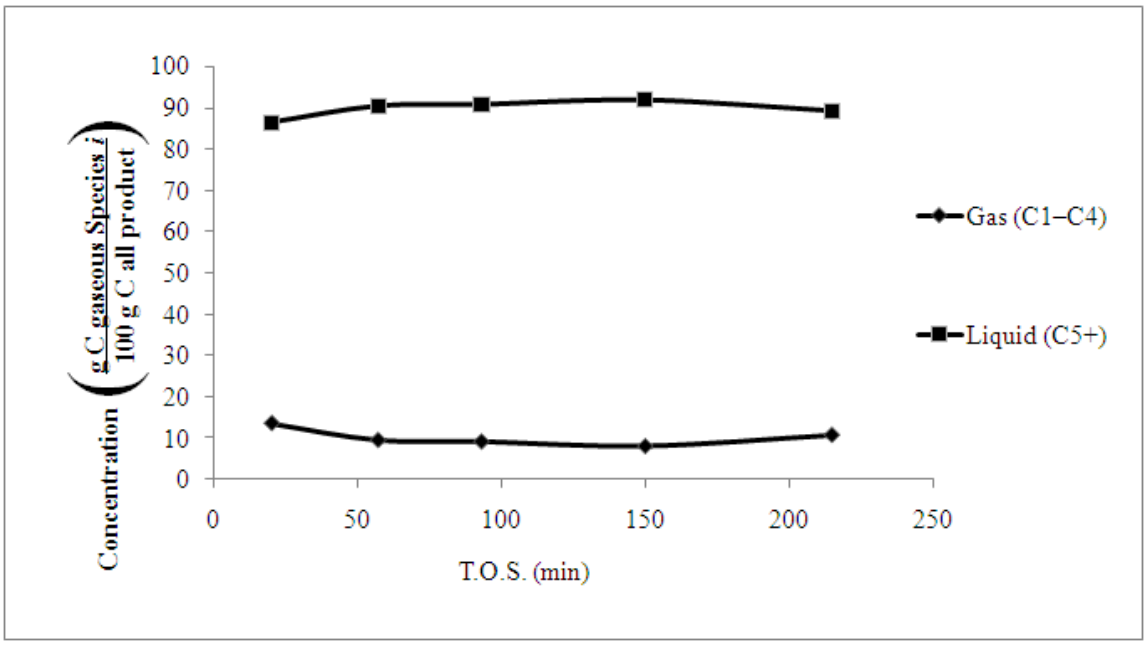

Figure 5.3. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (280), T = 415 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.4 shows the effect of high pressure for the reaction of acetone over HZSM-5 (280) on the conversion and the composition of gaseous and liquid reaction products (P = 7.8 atm (absolute), T = 410 °C, and WHSV = 9.48 h^{-1}). High pressure rapidly deactivates the catalyst. For instance, in Figure 5.4, the conversion decreased from 95% to 75% after 90 min, which may result from large molecules ($C11^{+}$) poisoning the catalyst.

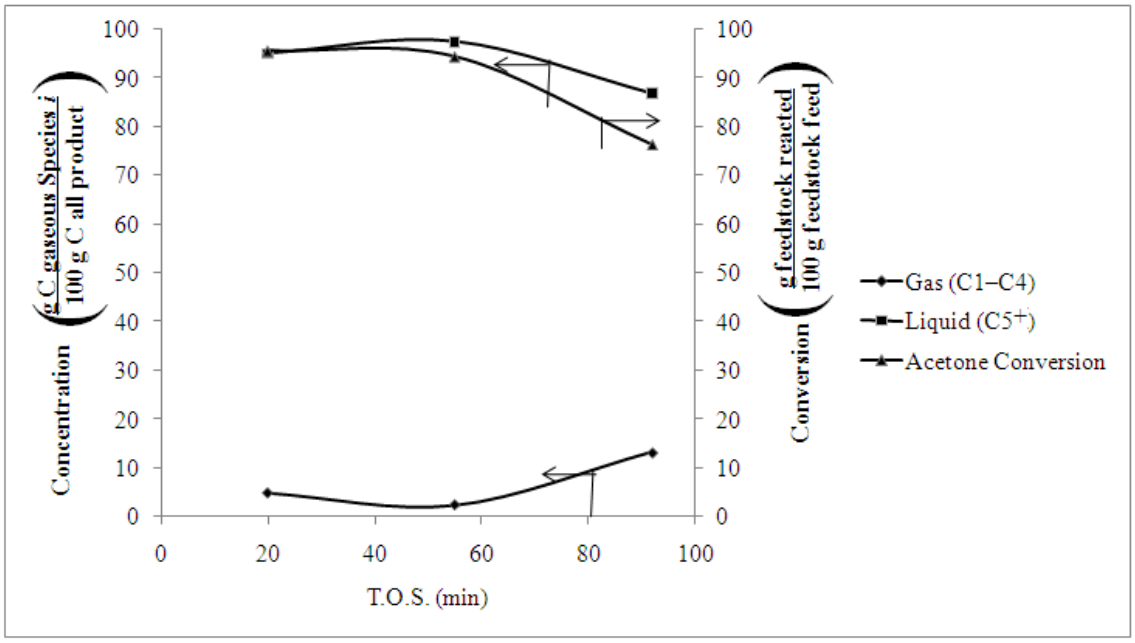

Figure 5.4. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (280), T = 415°C, WHSV = 1.3 h^{-1}, P = 7.8 atm (absolute).

Figure 5.5 shows the effect of co-feeding hydrogen in the reaction using a ratio of 0.34 mol H_2/mol acetone at T = 415 °C, P = 7.8 atm (absolute), WHSV=1.3 h^{-1}, and HZSM-5 (80). Because hydrogen inhibits catalyst coking, the product selectivity was more stable with time, so the catalyst did not deactivate. According to Bearez et al. (1983), hydrogen reduces the rate of coke formation on acid catalysts. Additionally, compared with Figure 5.1, the amount of gases decreased from 80% to 50%.

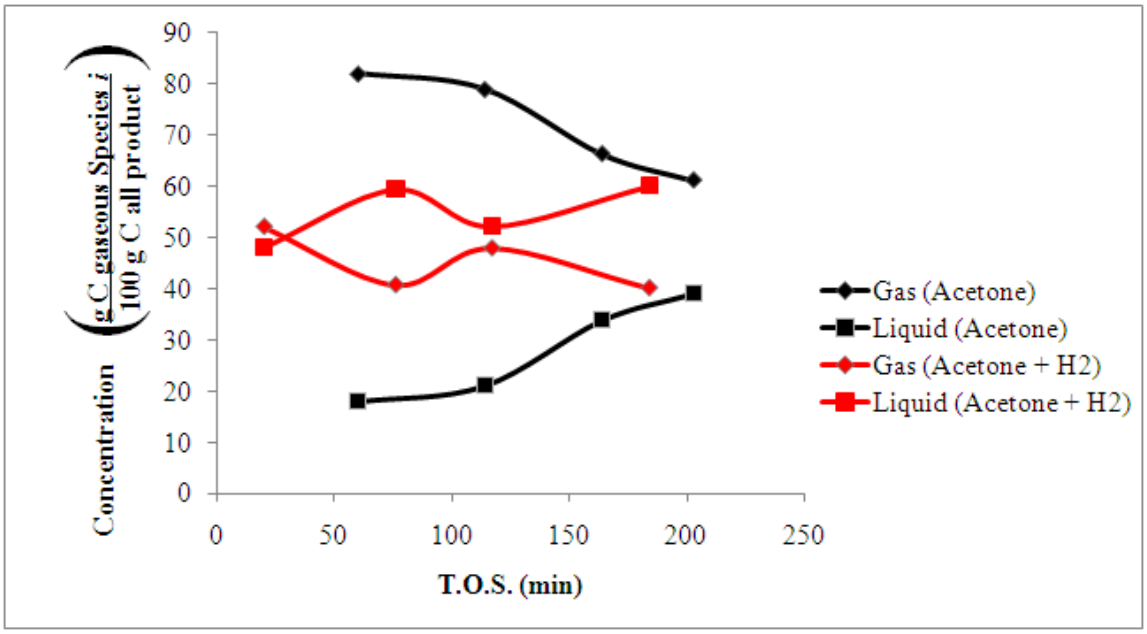

Figure 5.5. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415°C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute), mol H_2/mol acetone = 0.34.

5.2 Temperature Effects

Table 5.3 summarizes the three experiments that study the effect of temperature on reaction of acetone over HZSM-5 (80). The data presented in this set of experiments are average concentrations taken after feeding 30 mL of acetone. The average taken refers to the reaction product concentration at different times on stream.

Table 5.3 Experiments for the acetone reaction over HZSM-5 at different temperatures.

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	A1						
		350		A2						
		415		A6						
			0.3							
			0.5							
	280		0							
			03							
			0.5							
			1							
8	280		0							

Figure 5.6 shows the distribution of gases and liquid and the conversion of acetone for *T* = 305 to 415°C using catalyst HZSM-5 (80) and WHSV = 1.3 h^{-1}. The amount of gases increased from 20% (305°C) to 72% (415°C) whereas, the amount of liquids decreased from 80% (305°C) to 28% at (415°C). The conversion slightly increased from 90% to 100%.

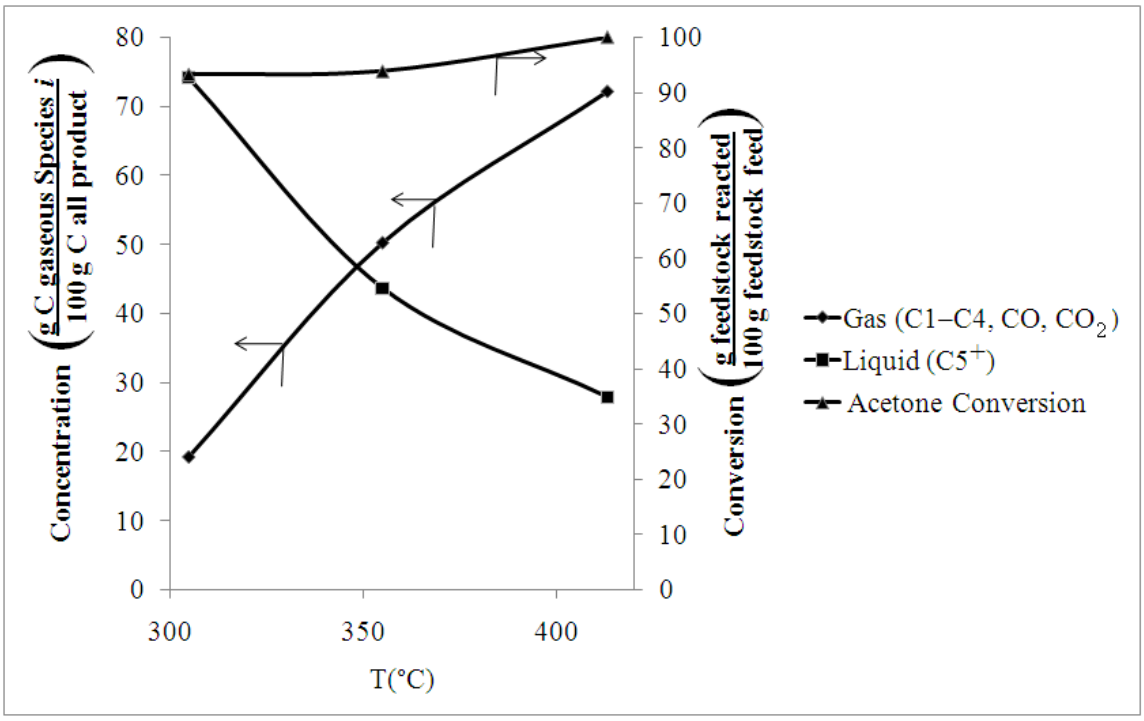

Figure 5.6. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.7 shows the product distribution of the gas phase at different temperatures for acetone over HZSM-5 (80). In both Figures 5.6 and 5.7, the selectivity for gaseous products increased with temperature. Propane, isobutene, and isobutylene were the most abundant compounds in the gas phase.

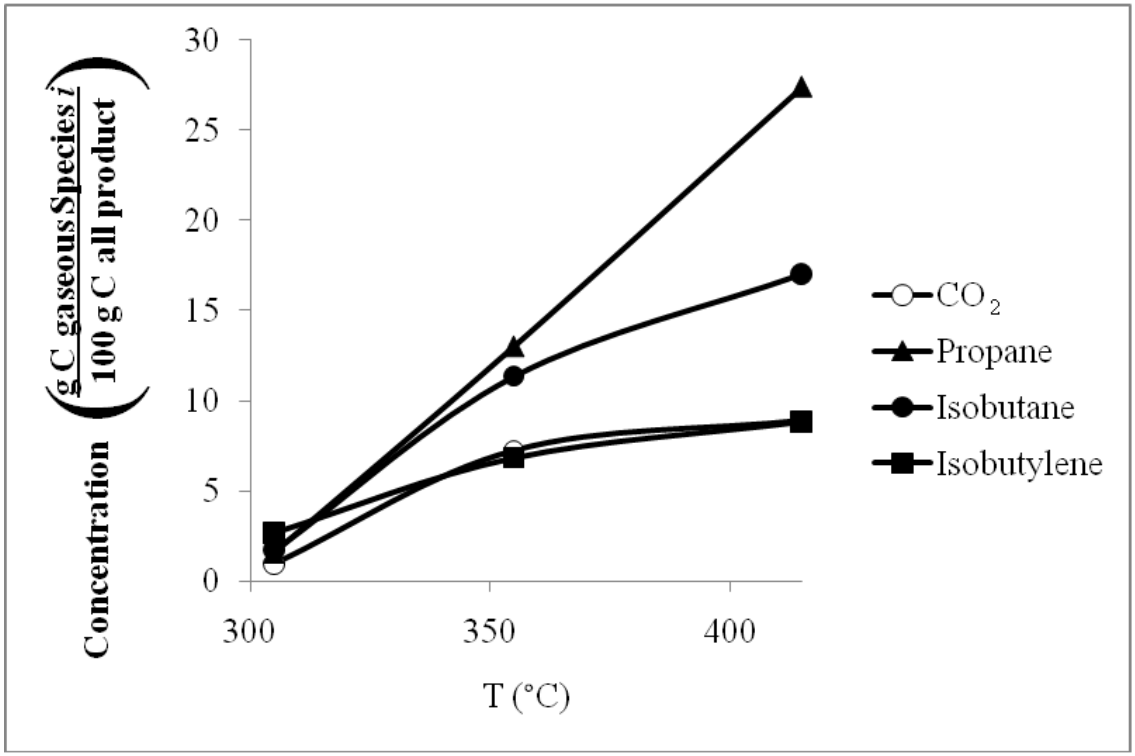

Figure 5.7. Product distribution of gases for the acetone reaction over HZSM-5 (80), WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.8 shows the type of liquid-phase products at T = 305, 350, and 415°C. Aromatics and oxygenated compounds were the only types of products in the liquid phase.

At T = 305°C, the most abundant component in the liquid phase was C9, mainly mesytilene (1,3,5-trimethylbenzene C_9H_{12}) and isophorone (1,1,3-trimethyl-3-cyclohexene-5-one $C_9H_{14}O$). The concentration of isophorone decreased from 15% to 0% when T increased from 305°C to 415°C and the concentration of C9 aromatics decreased from 25% (305°C) to 20% (400°C).

On the other hand, the concentration of C8 aromatics increases from 15% (305°C) to 40% (415°C), which is attributed to cracking of mesitylene (C9) into xylene. Kunyuan et al. (2007) reported the cracking of mesitylene over HZSM-5 at 480 °C and

showed the most abundant reaction product is xylene. According to Kunyuan et al. (2007), cracking benefits from increased temperature. For the three experiments at different temperatures, the amount of benzene is less than 5% of the liquid.

Furtheremore, it is noteworthy there is a Gaussian normal distribution of compounds centered on C9 (305°C) and C8 (415°C). This Gaussian distribution of products was not observed in the isopropanol reactions. Figure 5.8 also shows the most abundant compound for each carbon number. For example, at 305 °C and C9 fraction, the most abundant aromatic component is mesitylene; on the other hand at 415 °C and C8 fraction, the most abundant aromatic compound is para-xylene.

Tables 5.4, 5.5, and 5.6 show the liquid composition at three temperatures 305, 350, and 415°C, respectively. There were about 100 components for each sample; however, Tables 5.4, 5.5, and 5.6 show only the most abundant compounds. The total amount of all components for each table represents about 80% (wt) of the total amount of liquid products. The other components that represent 20% (wt%) are not shown in the table because they are so many and the concentration is less than 1% (wt). The balance of the distribution of liquid and gas is shown in Figure 5.1.

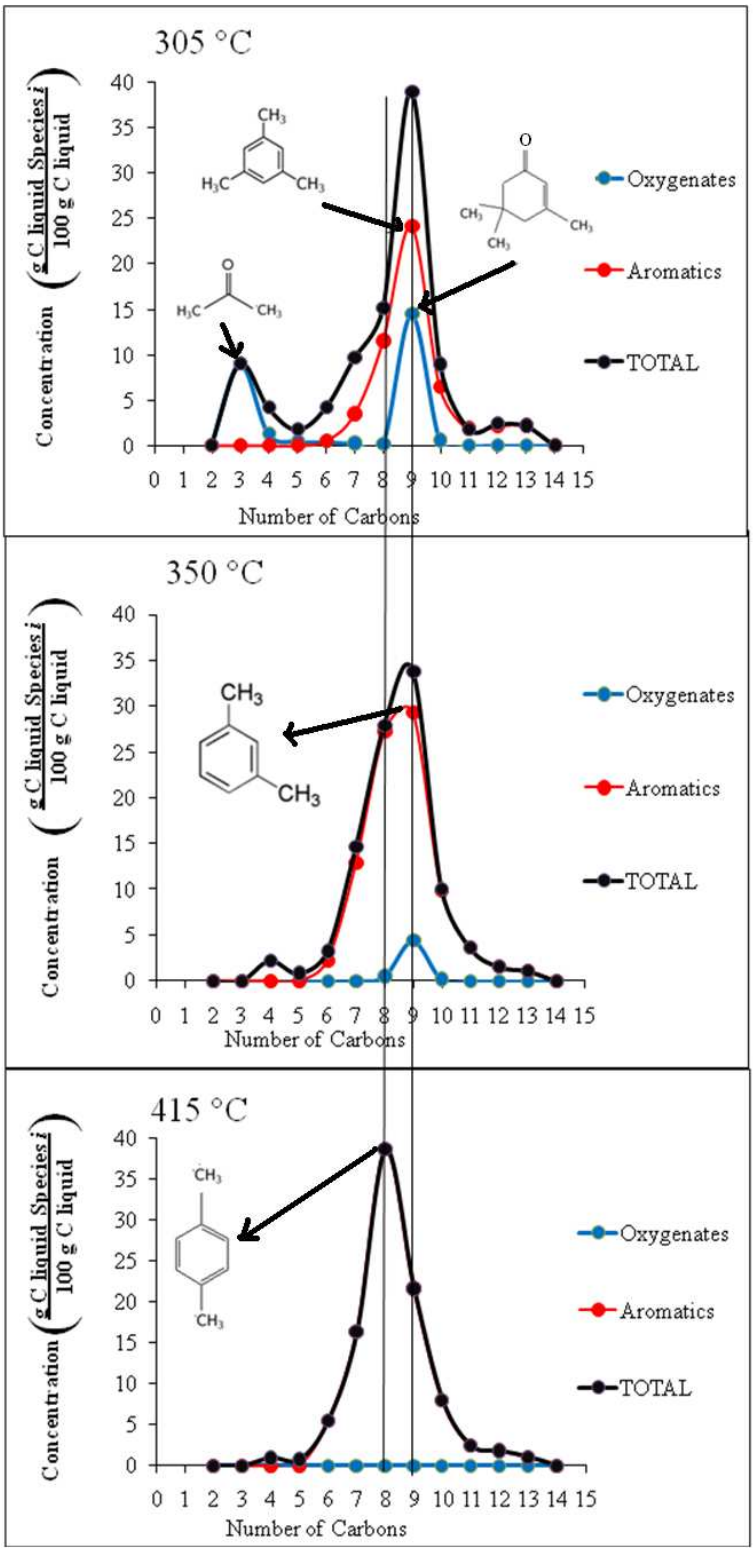

Figure 5.8. Liquid type product distribution of acetone reaction over HZSM-5 (80), P = 1 atm (absolute).

Table 5.4 Most abundant compound distribution for the acetone reaction over HZSM-5 (80), T = 305°C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Aromatics (g C liquid Species *i* /100 g C liquid)		Oxygenated (g C liquid Species *i* /100 g C liquid)		Others (g C liquid Species *i* /100 g C liquid)	
benzene, 1,3-dimethyl	10.5	2-cyclohexen-1-one, 3,5,5-trimethyl	14.1	cyclopropane, (1-methylethenyl)	2.4
mesitylene	8.3	2-propanone	9.0	cyclobutane, isopropylidene	2.2
benzene, 1-ethyl-2-methyl	8.2	2-butanone	1.2	cyclopropane, 1,2-dimethyl	1.3
benzene, 1,2,3-trimethyl	6.7			cyclopentene, 1,5-dimethyl	2.1
benzene, methyl	3.4			1-propene, 2-methyl	2.8
benzene, 1-methyl-3-propyl	1.6				
benzene, 1,2-diethyl	1.5				
benzene, 1,2,3,5-tetramethyl	2.1				
benzene, ethyl	0.9				
naphthalene, 1,2,3,4-tetrahydro-2	0.8				

Table 5.5 Most abundant compound distribution for the acetone reaction over HZSM-5 (80), T = 350 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Aromatics (g C liquid Species *i* /100 g C liquid)		Oxygenated (g C liquid Species *i* /100 g C liquid)		Others (g C liquid Species *i* /100 g C liquid)	
benzene, 1,3-dimethyl	18.0	2-cyclohexen-1-one, 3,5,5-trimethyl	10.5	propane, 2-methyl	1.5
benzene, methyl	12.3				
benzene, 1-ethyl-4-methyl	12.1				
benzene, 1,2,3-trimethyl	10.8				
benzene, 1,4-diethyl	6.6				
benzene, 1,2,3-trimethyl	4.0				
benzene, ethyl	3.0				
benzene, 2-ethyl-1,3-dimethyl	2.8				
benzene	1.7				
naphthalene, 1,5-dimethyl	1.5				
1H-indene, 2,3-dihydro-4-methyl	1.2				
benzene, 1,2,3,4-tetramethyl	1.1				
naphthalene, 1-methyl	1.0				

Table 5.6 Most abundant compound distribution for the acetone reaction over HZSM-5 (80), T = 415°C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Aromatics (g C liquid Species *i* /100 g C liquid)	
benzene, 1,4-dimethyl	30.3
benzene, methyl	16.3
benzene, 1,2,4-trimethyl	9.5
benzene, 1,3,5-trimethyl	8.6
benzene, 1,3-dimethyl	8.3
benzene	5.5
naphthalene, 2-methyl	1.5

5.3 WHSV Effects

Twenty experiments were performed to study the effect of WHSV. Table 5.7 shows the conditions for this set of experiments. All experimental data are based on the average product analysis after feeding 30 mL of acetone.

Figure 5.9 shows the acetone conversion at different WHSV (1.32, 2.63, 3.95, 5.27, 6.58 and 7.9 h^{-1}) for HZSM-5 (80), T = 415 °C, and P = 1 atm (absolute). As expected, the acetone conversion is lower at high WHSV, dropping from 100% to 87%. The amount of gas decreases, because there is not enough residence time for oligomerization at high WHSV. The tendency is for all gaseous products to decrease at high WHSV.

Table 5.7 Set of experiments for the acetone reaction over HZSM-5 at different WHSV.

P	Catalyst	T	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0							
		350		A2	A3	A4	A5			
		415		A6	A7	A8	A9	A10	A11	
			0.3							
			0.5							
	280		0	A18	A19	A20	A21	A22		
			03							
			0.5							
			1							
7.8	280		0	A30		A31	A32		A33	A34

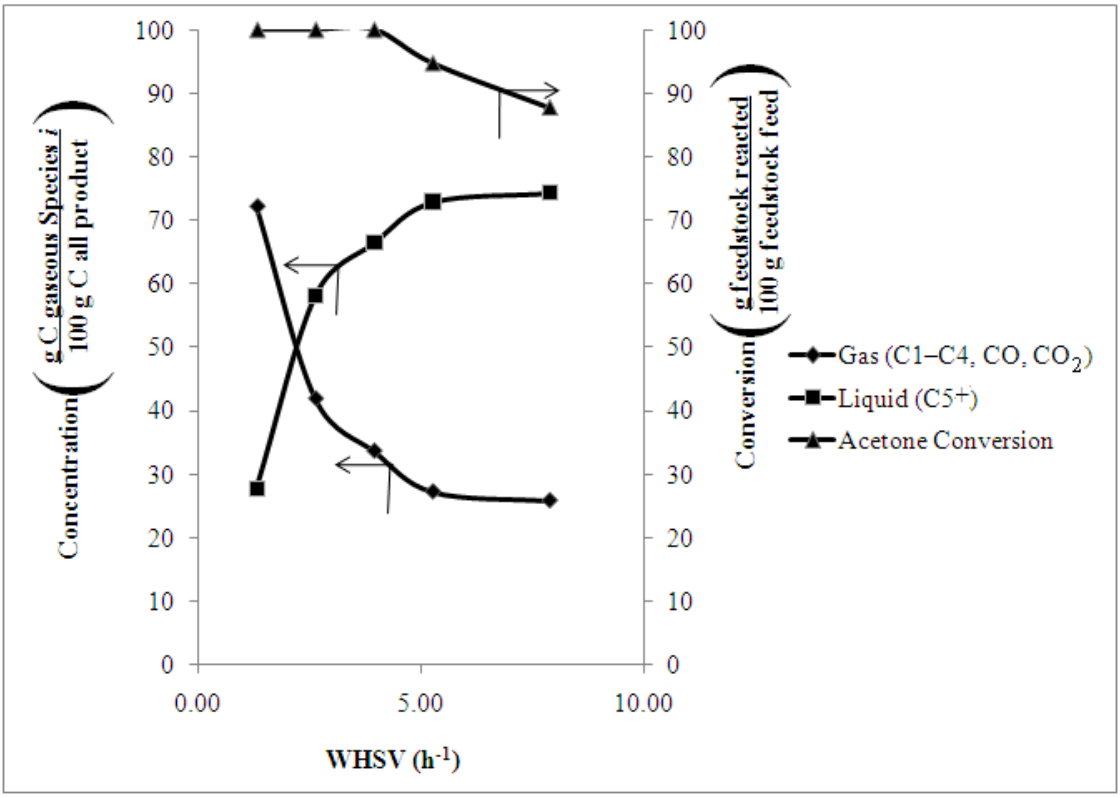

Figure 5.9. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415 °C, P = 1 atm (absolute).

Figure 5.10 shows the gaseous product distribution at different WHSV for acetone reacting over HZSM-5 (80) at T = 415 °C. Only gases with concentrations above 5 wt% are reported. The most abundant gases are propane and isobutane. The tendency is for all gaseous products to decrease at high WHSV.

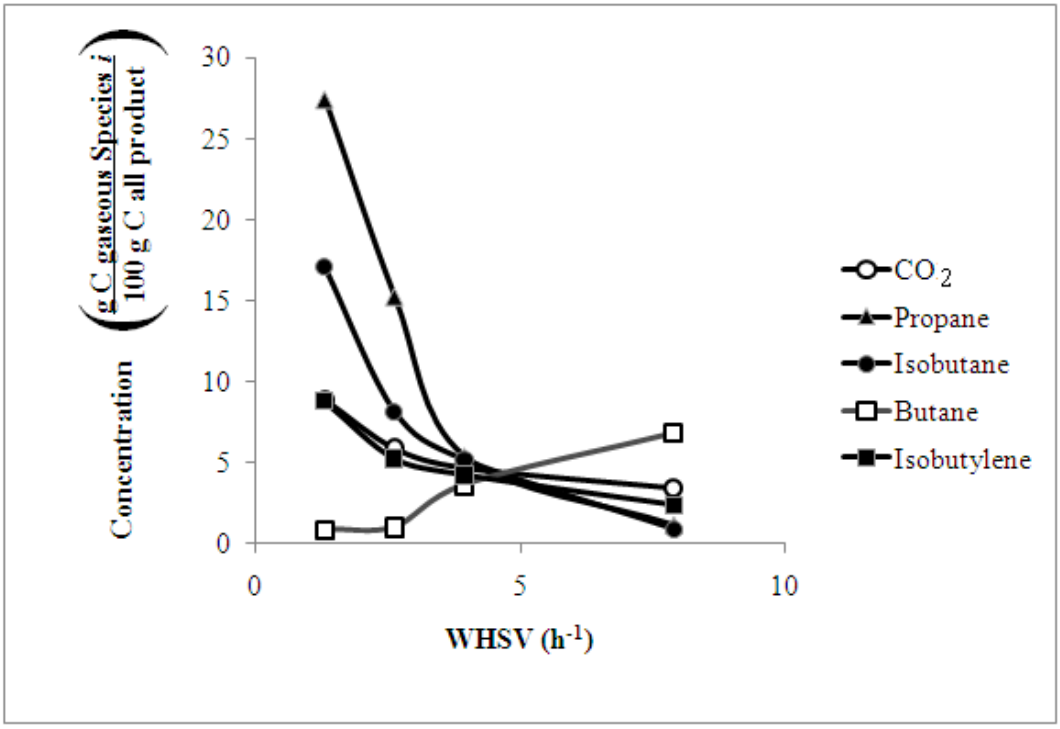

Figure 5.10. Product distribution of gases for the acetone reaction over HZSM-5 (80), T = 415°C, P = 1 atm (absolute).

Figure 5.11 shows the acetone conversion at different WHSV (1.32, 2.63, 3.95, 5.27, and 6.58 h^{-1}) for HZSM-5 (80) at T = 350 °C and P = 1 atm (absolute). As expected, the acetone conversion is lower at higher WHSV.

Comparing Figures 5.9 and 5.11, it is apparent that at the same WHSV, the conversion at 350 °C is lower than the conversion at 415 °C. At 415 °C, the conversion dropped from 100% (1.3 h^{-1}) to 87% (7.9 h^{-1}). In contrast, at 350 °C, the conversion dropped from 93% (1.3 h^{-1}) to 78% (6.5 h^{-1}). The amount of gases also decreased at high WHSV.

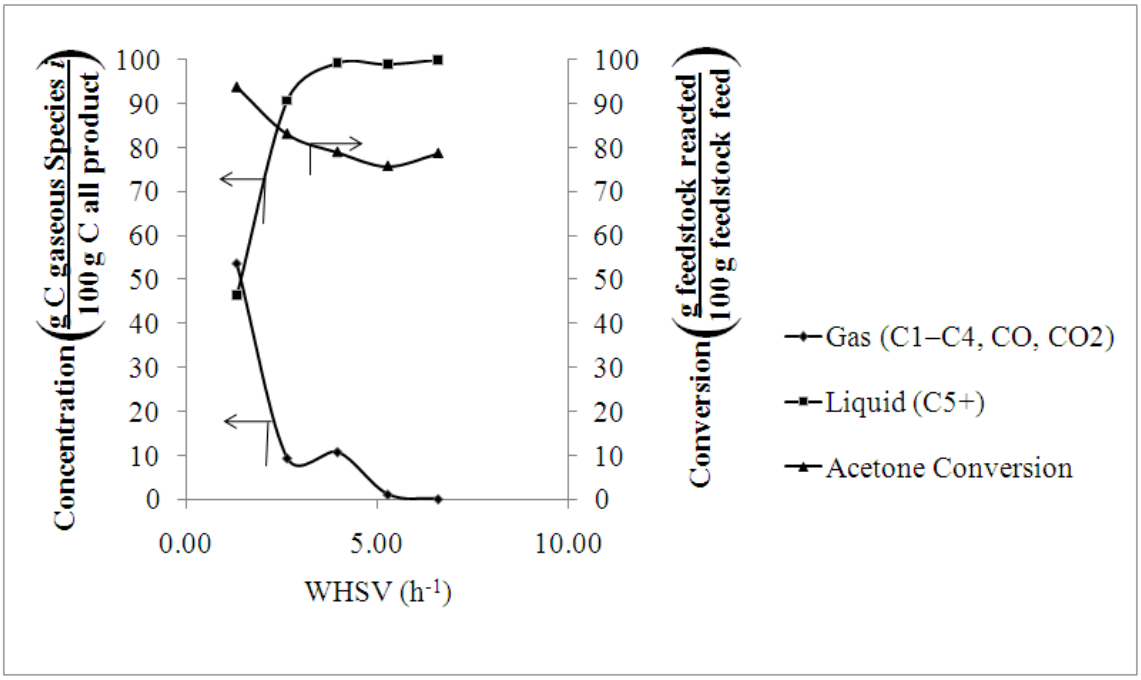

Figure 5.11. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 350°C, P = 1 atm (absolute).

Figure 5.12 shows the acetone conversion at different WHSV (1.3, 2.63, 3.95, and 5.27 h^{-1}) using HZSM-5 (280) at T = 415 °C and P = 1 atm (absolute). As expected, the acetone conversion is lower at higher WHSV. The gases decreased at high WHSV; at 1.3 h^{-1}, the concentration of gases was 25%, and at 5.2 h^{-1} was only 5%. HZSM-5 (280) has fewer acid sites in its structure, so it is less reactive; therefore, the conversion for HZSM-5 (280) is less than the conversion for HZSM-5 (80).

Figure 5.13 shows the acetone conversion at different WHSV (1.6, 4.0, 5.5, 7.9, 9.5, and 11.9 h^{-1}) using HZSM-5 (280) at T = 415°C and P = 7.8 atm (absolute). As expected, the acetone conversion is lower at high WHSV. High pressure does not favor the reaction; the conversion at high pressure (Figure 5.13) is lower than the conversion at atmospheric pressure (Figure 5.12).

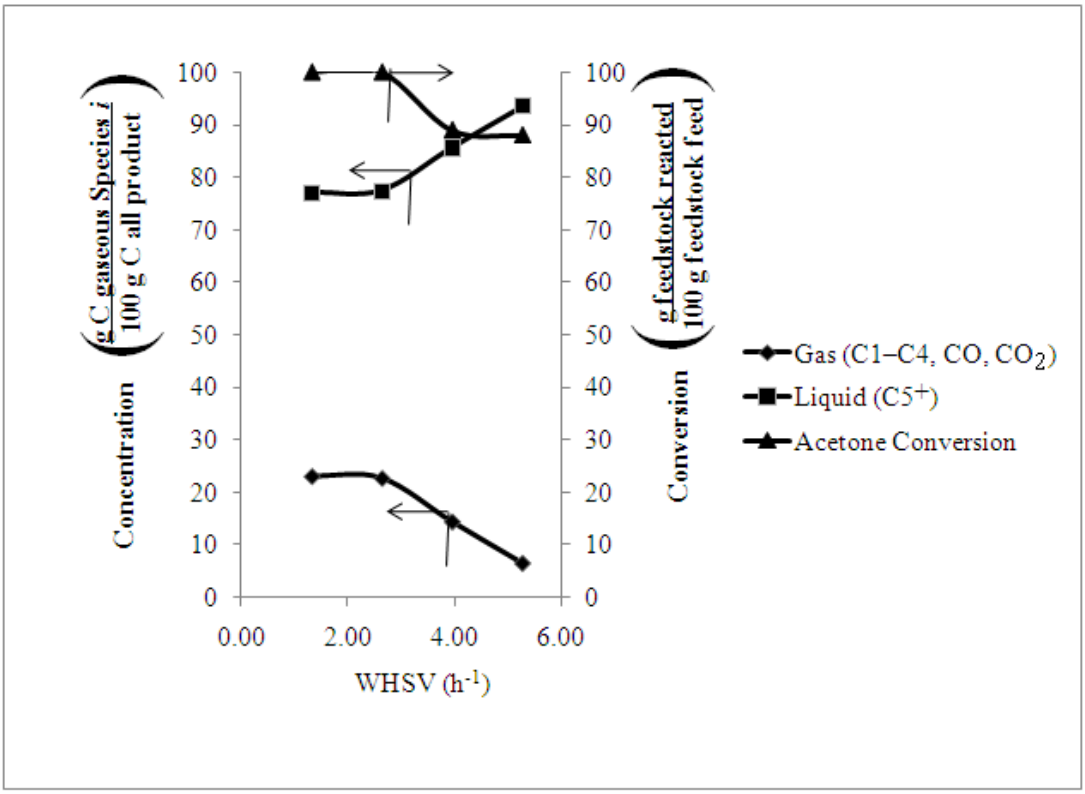

Figure 5.12. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (280), T = 415°C, P = 1 atm (absolute).

Figure 5.14 illustrates the types of liquid-phase products at different WHSV (1.3, 2.63, 3.95 and 5.27 h^{-1}) using HZSM-5 (280) at T = 415°C and P = 1 atm (absolute). Aromatic compounds are the most abundant products in the hydrocarbon phase.

There are some oxygenated compounds at C3 and C9. C3 is unreacted acetone that dissolves in the hydrocarbon phase. C9 is the oxygenated compound isophorone (1,1,3-trimethyl-3-cyclohexene-5-one, $C_9H_{14}O$). At low WHSV (1.3 h^{-1}), the most abundant component in the liquid phase is C8. When the WHSV increases, the most abundant compound in the liquid phase is C9. For example, in Figure 5.14 at WHSV = 1.32 h^{-1}, the most abundant compound is C8 and at WHSV = 5.37 h^{-1} the most abundant component is C9. This may result because mesitylene does not have the time to crack at high WHSV and form xylenes or toluene. This effect was also observed at low

temperatures.

Figures 5.15 illustrates the types of liquid-phase products at different WHSV (1.3, 2.63, 3.95, and 5.27 h^{-1}) using HZSM-5 (80) and T = 415 °C and P = 1 atm (absolute). Comparing Figures 5.14 and 5.15, it is apparent that the effect of increasing WHSV on HZSM-5 (80) is similar to HZSM-5 (280) which at high values of WHSV there is less conversion, carbon distribution C9-centered and oxygenates presence in the liquid phase.

HZSM-5 (80) is more reactive than HZSM-5 (280). For example, at WHSV= 5.97 h^{-1} the concentration of unreacted acetone is zero with HZSM-5 (80); however, with HZSM-5 (280), the concentration of unreacted acetone is 10%.

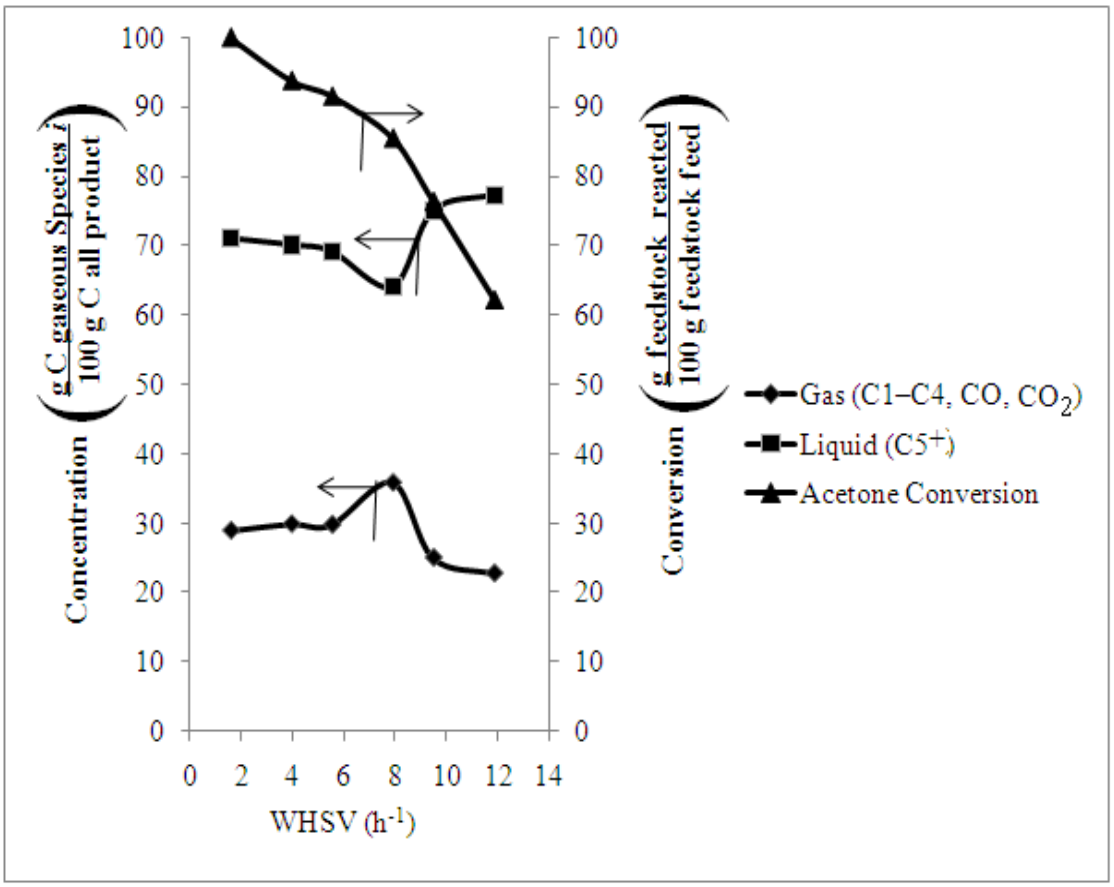

Figure 5.13. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415°C, P = 7.8 atm (absolute).

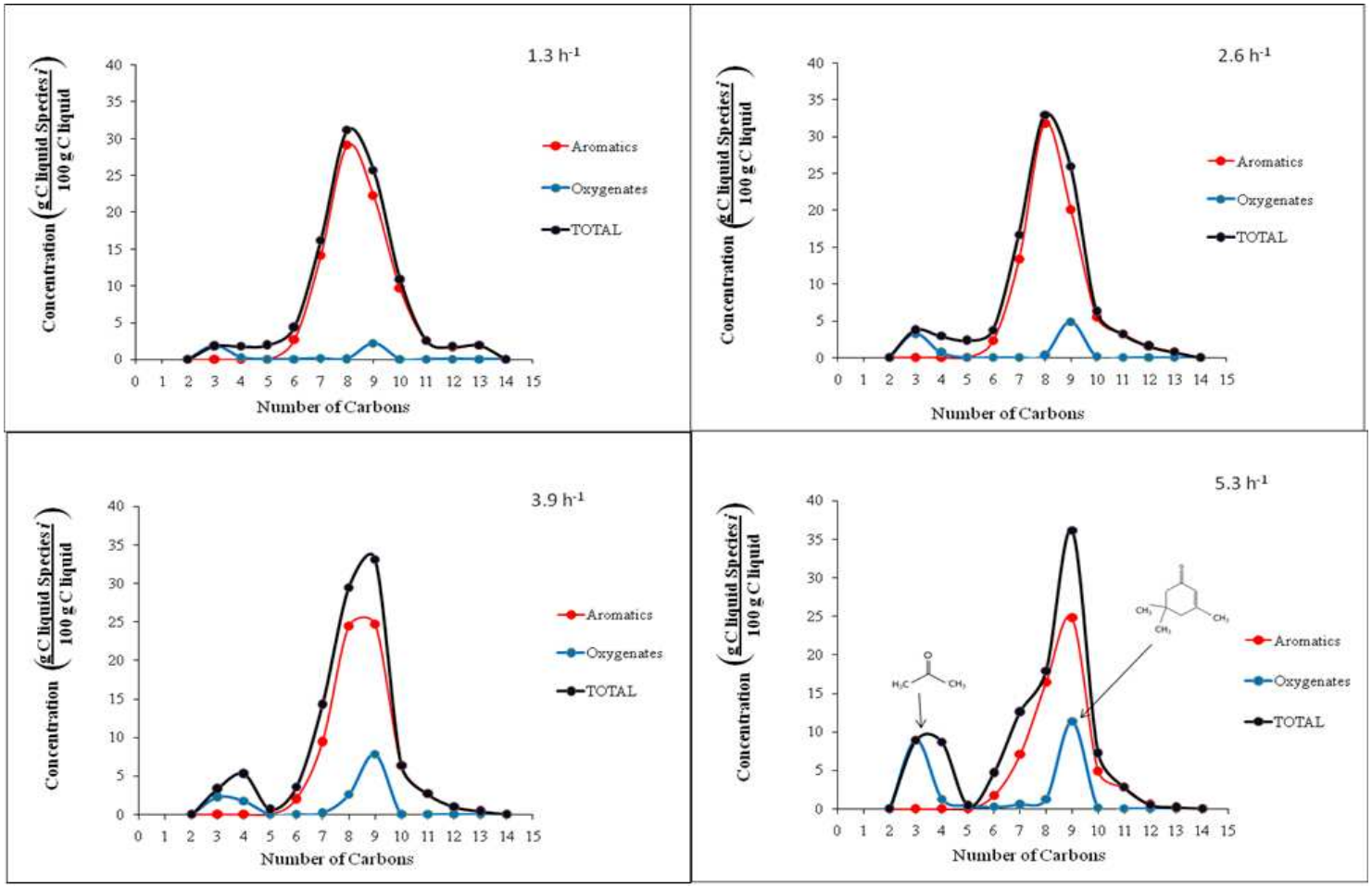

Figure 5.14. Liquid product distribution of acetone reaction over HZSM-5 (280), P = 1 atm (absolute), T = 415 °C at different WHSV.

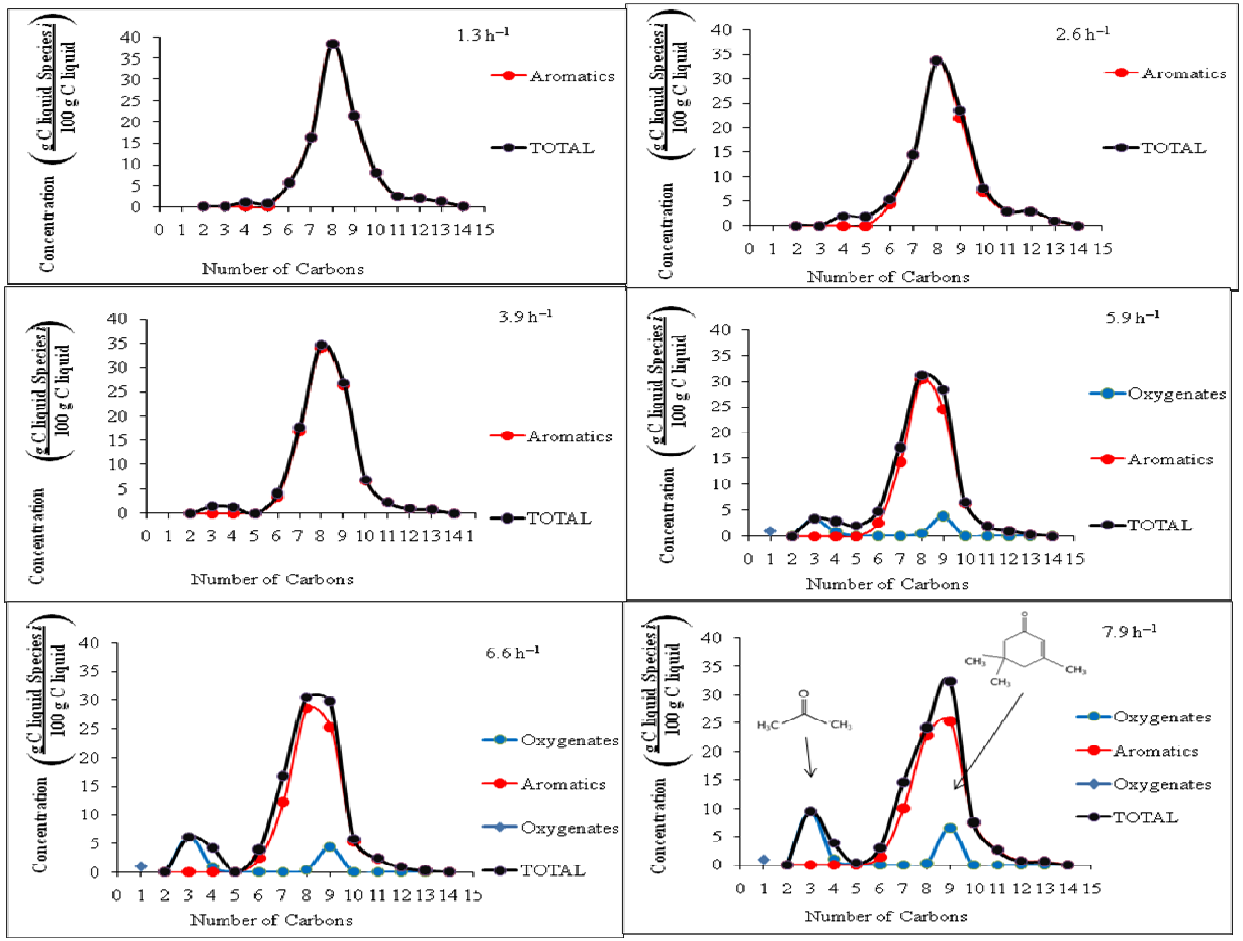

Figure 5.15. Liquid product distribution of acetone reaction over HZSM-5 (80), T = 415°C, P = 1 atm (absolute) at different WHSV.

5.4 Effect of Hydrogen Ratio

This section reports the effect of adding hydrogen to the acetone reaction using HZSM-5 (80) and (280). Table 5.8 shows the nine experiments.

Figure 5.16 shows the acetone reaction products at different H_2 ratios using HZSM-5 (80) at T = 415 °C, WHSV = 1.3 h^{-1}, and P = 1 atm (absolute). At higher H_2 ratios, the gas yield decreases.

Table 5.8. Set of experiments for the acetone reaction over HZSM-5 at different acetone hydrogen ratios.

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0							
		350								
		415								
			0.3	A12		A14				
			0.5	A15		A17				
	280		0							
			03	A23						
			0.5	A24	A25					
			1	A27	A28					
8	280		0							

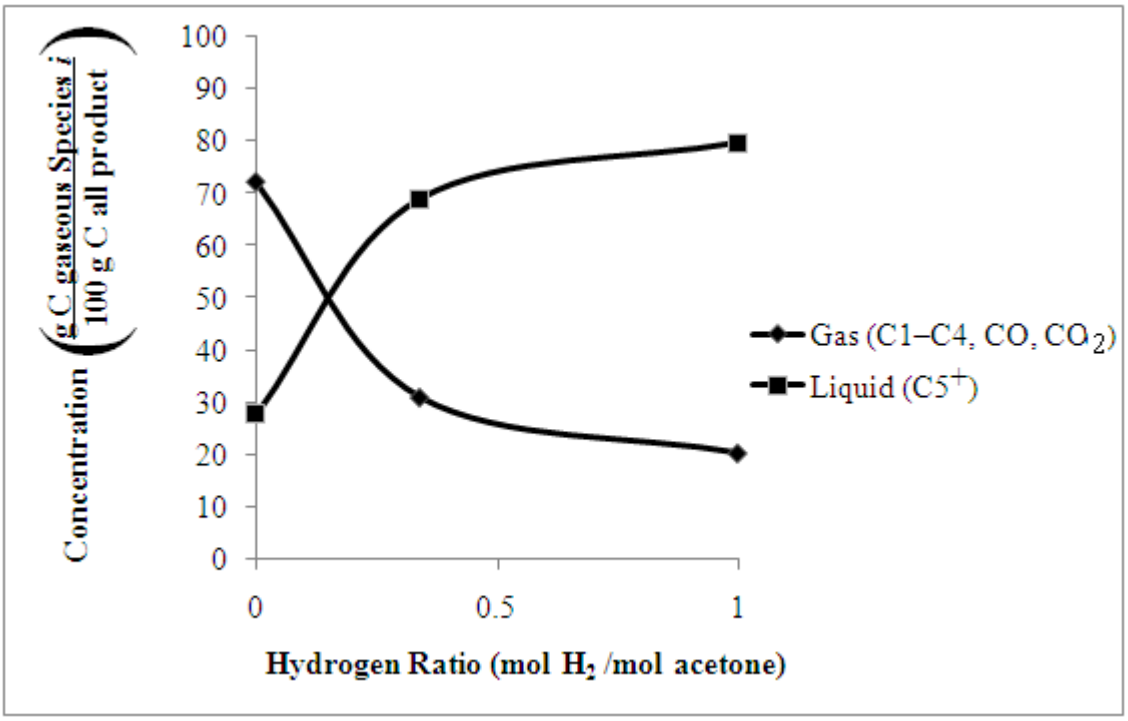

Figure 5.16. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.17 shows the gaseous product distribution at different molar ratios of hydrogen to acetone for acetone reacting over HZSM-5 (80) at T = 415 °C, WHSV = 1.3 h^{-1}, and P = 1 atm (absolute). Only gases with concentrations over 5 g C gaseous Species i /100 g C all product are reported. The most abundant gases are propane and isobutane. At higher hydrogen ratios, gaseous products tend to decrease.

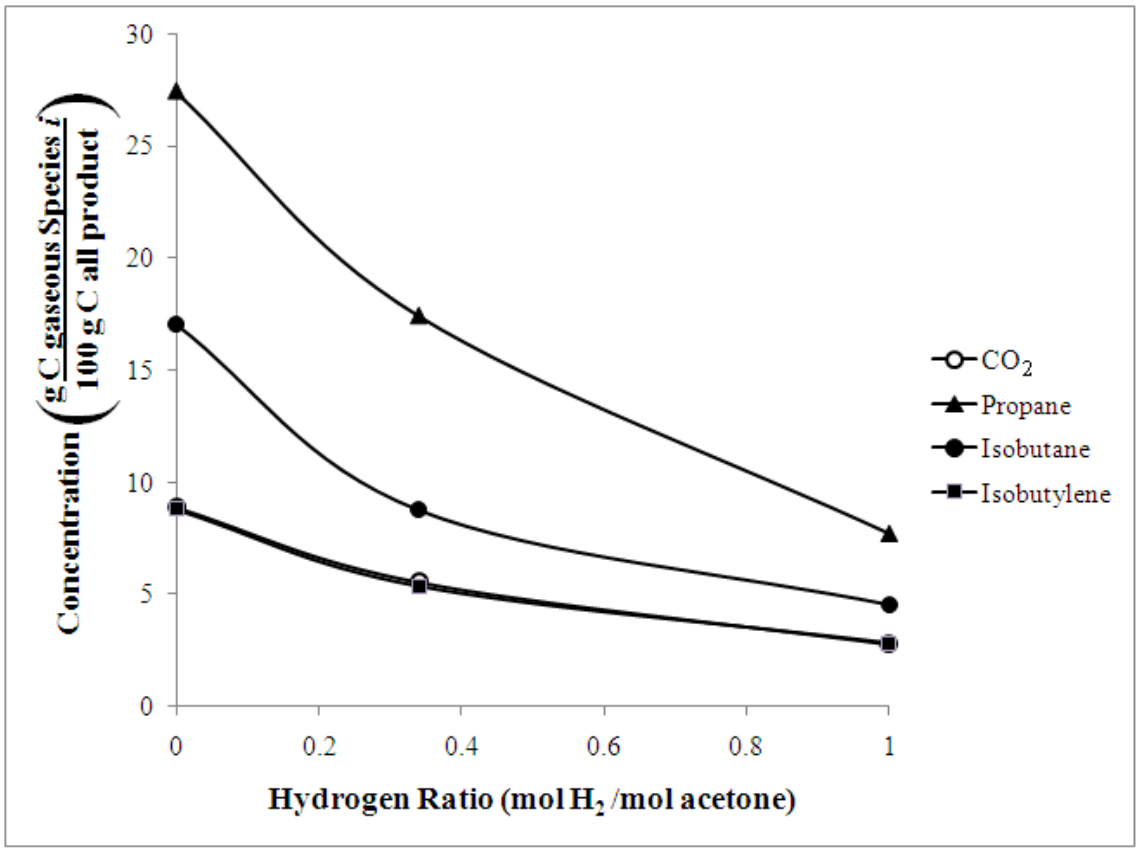

Figure 5.17. Product distribution of gases for the acetone reaction over HZSM-5 (80), T = 415°C, WHSV=1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.18 shows the product concentration of liquid and gas at different feed H_2 ratios for acetone reacting over HZSM-5 (80) at T = 415 °C, WHSV = 3.95 h^{-1}, and P = 1 atm (absolute). Adding hydrogen decreases the amount of gases at high H_2 ratios.

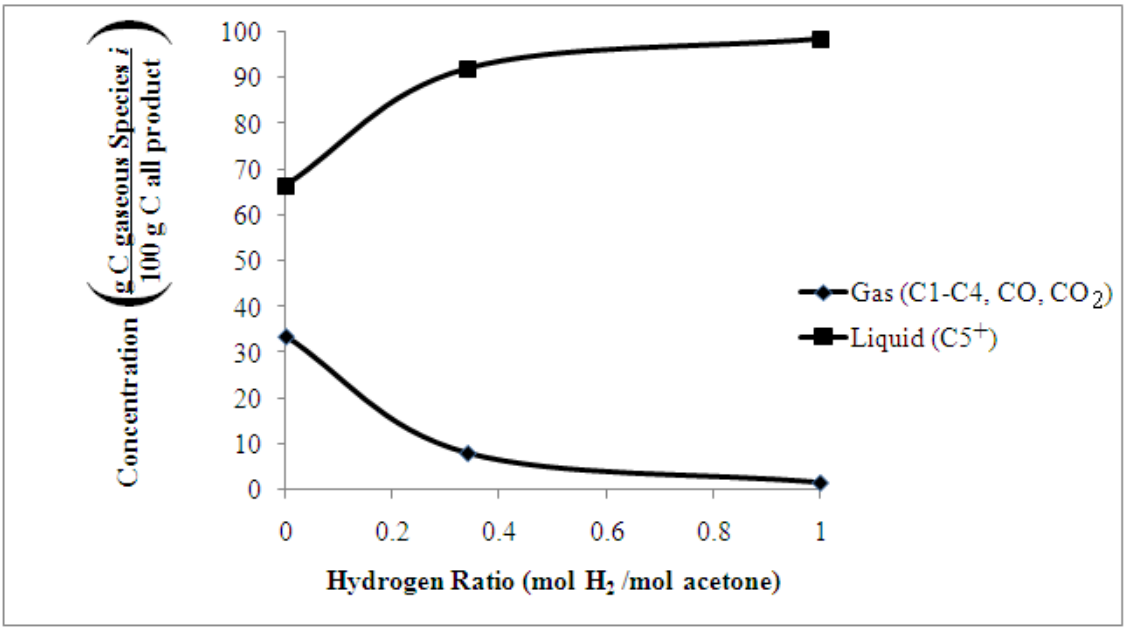

Figure 5.18. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (80), T = 415°C, WHSV = 3.95 h^{-1}, P = 1 atm (absolute).

Figures 5.19 and 5.20 shows the product concentration of liquid and gas at different H_2 ratios for acetone reacting over HZSM-5 (280). The gaseous product was nearly constant at different H_2 feed ratios. In contrast to HZSM-5 (80), with HZSM-5 (280), there is no effect of adding hydrogen.

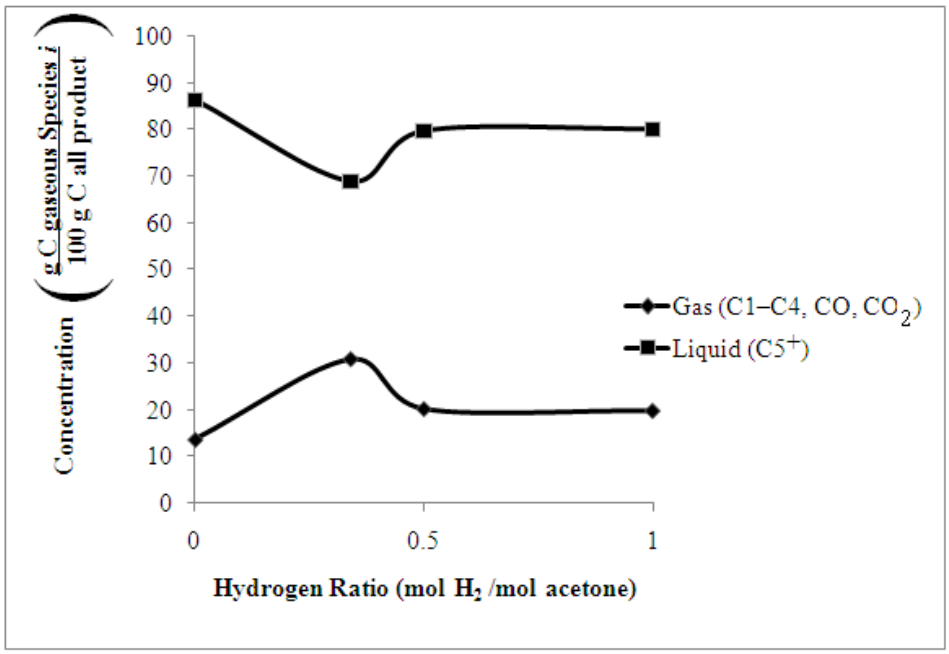

Figure 5.19. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (280), T = 415°C, WHSV = 2.6 h^{-1}, P = 1 atm (absolute).

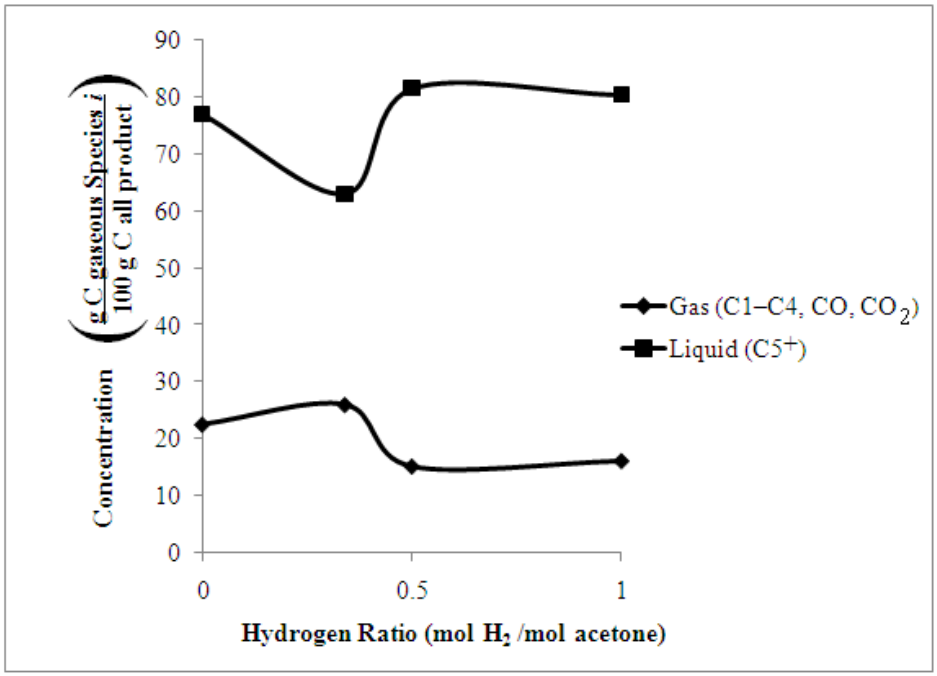

Figure 5.20. Product distribution of gases and liquids for the acetone reaction over HZSM-5 (280), T = 415°C, WHSV=1.3 h^{-1}, P = 1 atm (absolute).

Figure 5.21 illustrates the liquid-phase products at different H_2 ratios using HZSM-5 (80) at T = 415°C, WHSV = 1.3 h^{-1}, and P = 1 atm (absolute). Aromatics are the only products in the hydrocarbon phase. The liquid-phase products are not affected by adding hydrogen to the reaction.

Table 5.9 shows the most abundant product components for the acetone reaction at different H_2 ratios. The concentration of components does not change significantly at different H_2 ratios. Figure 5.22 shows the reaction path most probable for the acetone reaction over HZSM-5 according to the results obtained. Some of the intermediate reactions were taken from (Salvapati et al. 1989). The main products observed in the experiment with HZSM-5 are summarized in the scheme of reaction in Figure 5.22.

Finally, compared to isopropanol, acetone only produces aromatic compounds in the liquid hydrocarbon phase. Higher temperatures (more than 400 °C) produce a C8-centered liquid carbon distribution and 100% conversion. Acetone is more reactive with HZSM-5 (80) than HZSM-5 (280). HZSM-5 (80) gives more acetone conversion at the same conditions (T, WHSV) than HZSM-5 (280). However, HZSM-5 (280) is more stable because HZSM-5 (80) deactivates more quickly. At high pressure, acetone conversion over HZSM-5 (280) is lower than at atmospheric pressure because the catalyst rapidly deactivates. Adding hydrogen to the acetone reaction inhibits the formation of coke and reduces the concentration of gaseous products.

In conclusion, the objective to produce a mixture similar to commercial gasoline was not achieved; however, some compounds obtained from the acetone reaction over HZSM-5 and commercial gasoline are the same, such as aromatics. The best conditions for acetone are T = 415 °C, WHSV = 3.95 h^{-1}, P = 1 atm (absolute), catalyst = HZSM-5 (80), and no hydrogen. These conditions of temperature, WHSV, and pressure allow a better conversion, less gas, and less deactivation of catalyst. HZSM-5 (80) is better because it is more reactive and ensures no oxygenates in the liquid phase. Hydrogen reduces the amount of gases; however, it does not affect the composition of the hydrocarbon liquid.

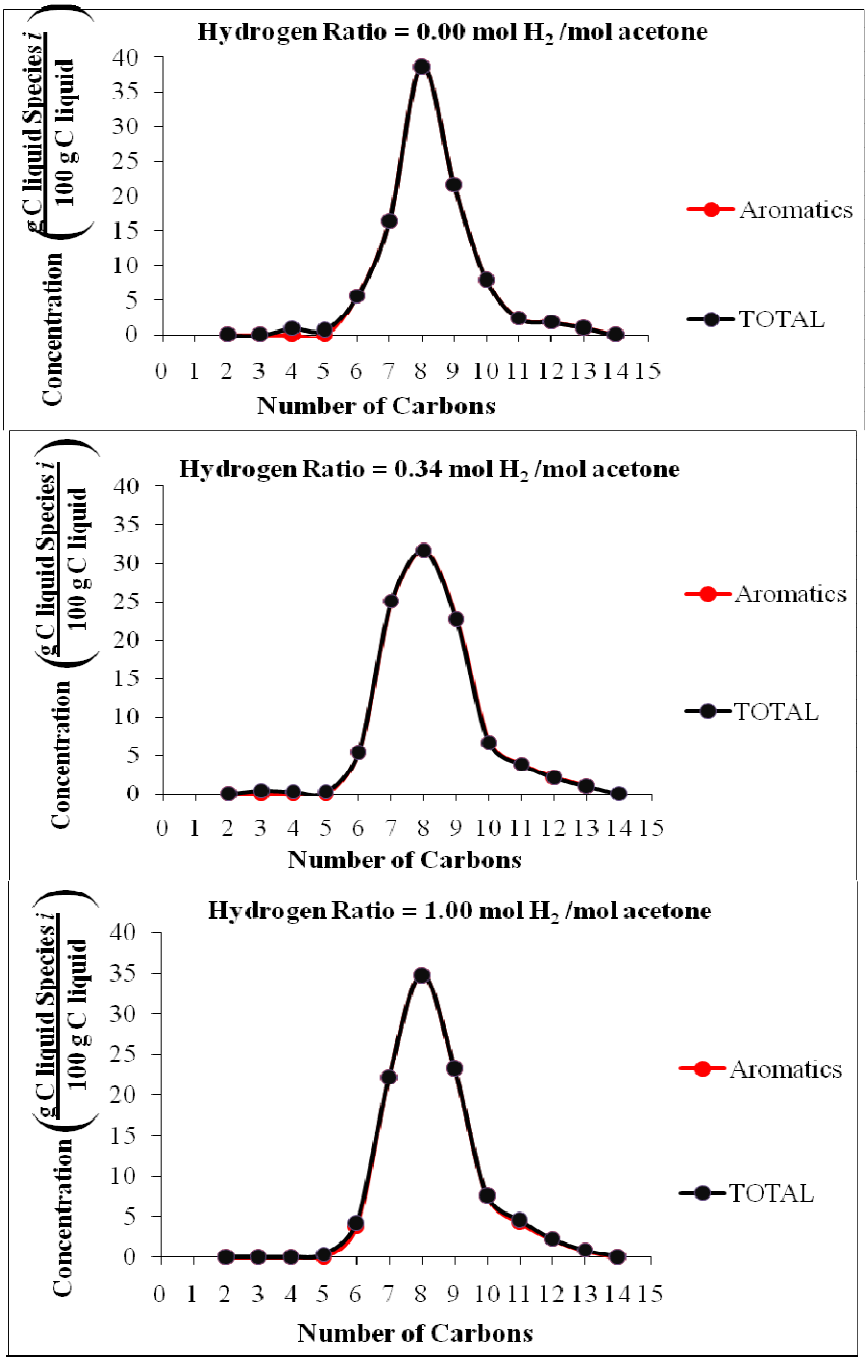

Figure 5.21. Liquid product distribution of acetone reaction over HZSM-5 (80), T = 415 °C, WHSV = 1.3 h^{-1}, P = 1 atm (absolute).

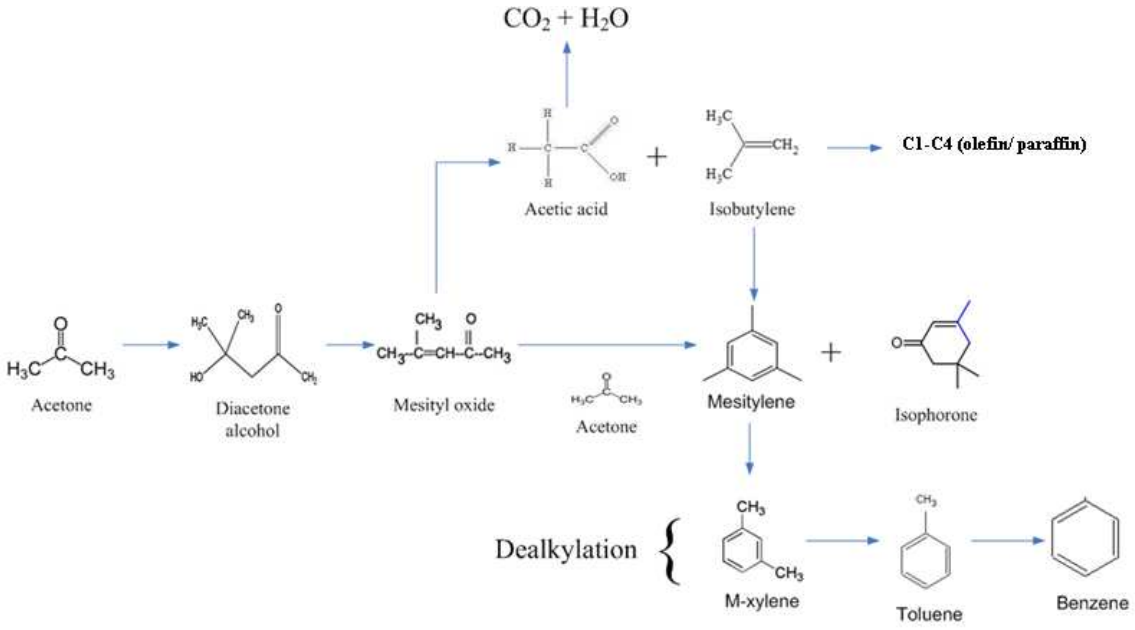

Figure 5. 22. Formation of reaction products in the acetone reaction over HZSM-5.

Table 5.9 Compound distribution for the acetone reaction over HZSM-5 (80) at different hydrogen ratios for T = 415°C, WHSV = 1.3 h^{-1}, P = 1atm (absolute).

	Hydrogen ratio (mol H_2/ mol acetone)		
	0	0.34	1
	Aromatic (g C liquid Species *i* /100 g C liquid)	Aromatic (g C liquid Species *i* /100 g C liquid)	Aromatic (g C liquid Species *i* /100 g C liquid)
benzene, 1,4-dimethyl	30.34	30.24	32.28
benzene, methyl	16.38	25.07	21.44
benzene, 1,2,4-trimethyl	9.59	8.94	5.46
benzene, 1,3,5-trimethyl	8.63	6.32	9.54
benzene	5.54	4.48	3.77
naphthalene, 2-methyl	1.54		

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

This study investigated the reaction of isopropanol and acetone over different types of HZSM-5 zeolites. For isopropanol, the effect of temperature and WHSV were evaluated. For acetone, the effect of temperature, WHSV, catalyst, pressure, and hydrogen co-feed were studied.

Over HZSM-5 the isopropanol reaction is sensitive to temperature and WHSV. At higher temperatures, more gaseous products are obtained. The WHSV determines the carbon number distribution. High WHSV gives high concentration of $C6^{+}$ olefins whereas low WHSV gives high concentrations of C9 aromatics. During the first 6 hours, there was no catalyst deactivation of the isopropanol reaction.

For the acetone reaction, temperatures above 400 °C are needed to get 100% conversion. Gaseous products are more abundant at high temperatures.

Acetone is more reactive with HZSM-5 (80) than HZSM-5 (280). HZSM-5 (80) gives more acetone conversion at the same conditions (*T*, WHSV) than HZSM-5 (280). However, HZSM-5 (280) is more stable with time because HZSM-5 (80) deactivates more quickly.

At high pressure, the conversion of acetone over HZSM-5 (280) is lower than at atmospheric pressure because the catalyst rapidly deactivates.

Adding hydrogen to the acetone reaction inhibits the formation of coke and reduces the concentration of gaseous products.

Figures 6.1 and 6.2 show the mass balances for isopropanol and acetone reaction at the recommended operating conditions.

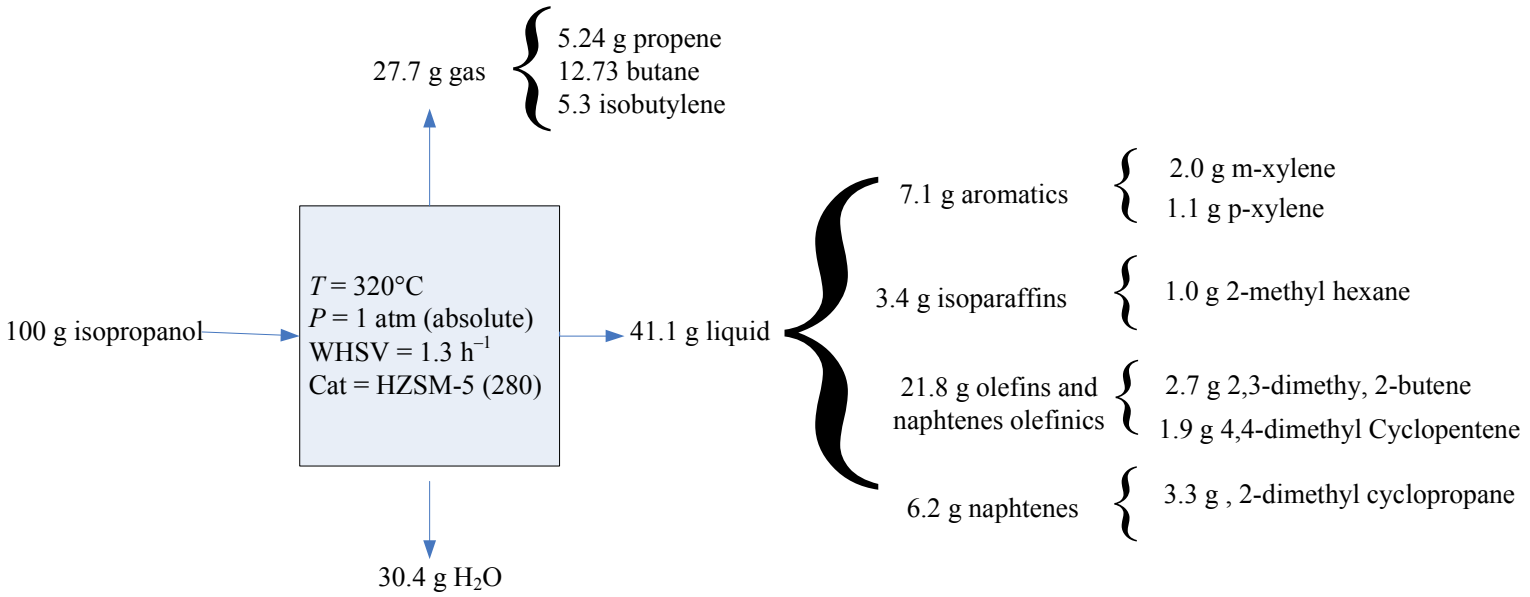

Figure 6.1. Mass balance for isopropanol reaction at recommended operating conditions.

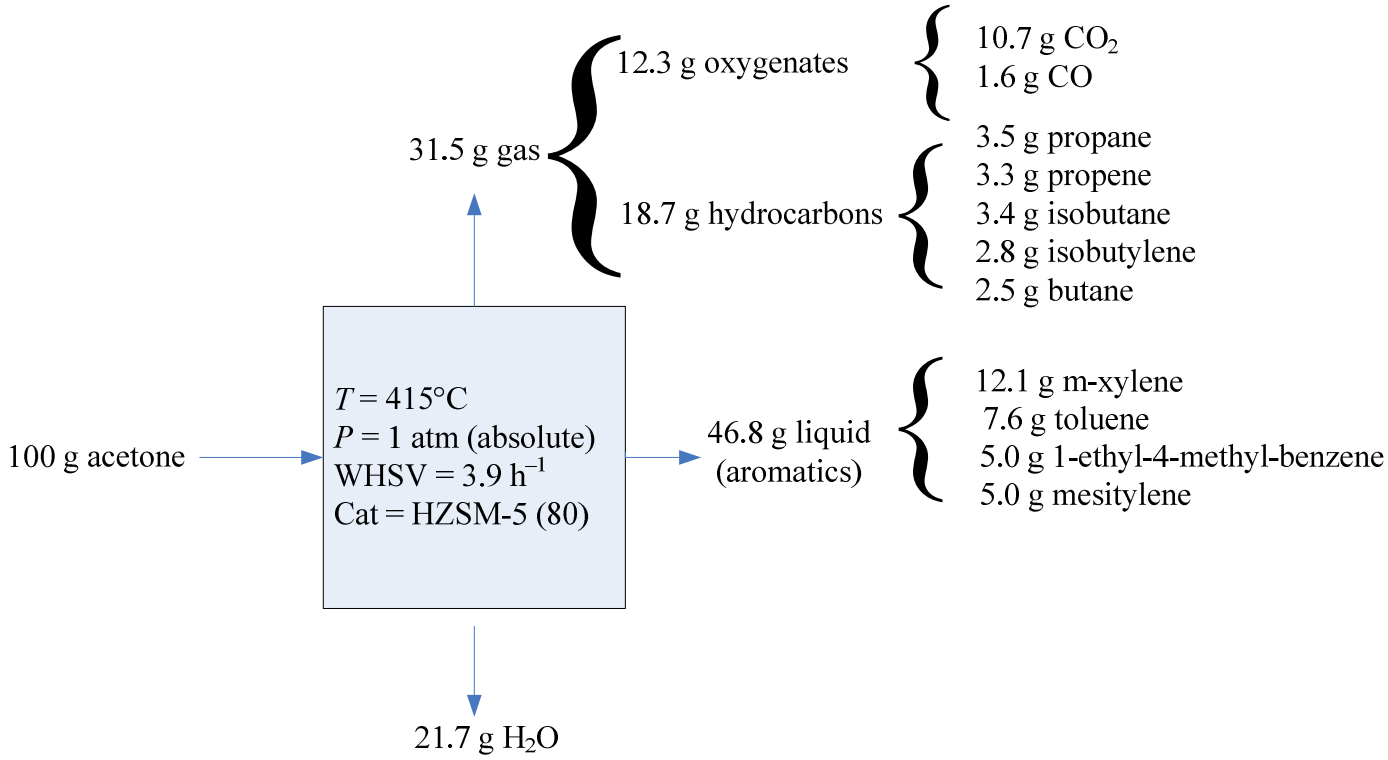

Figure 6.2. Mass balance for acetone reaction at recommended operating conditions.

CHAPTER VII

FUTURE STUDIES

In the future, the following studies should be performed:

1) Add hydrogen to the acetone reaction at high pressure to see if hydrogen reacts with the acetone.
2) Add hydrogen to the isopropanol reaction to reduce formation of olefins.
3) Perform kinetic studies of isopropanol and acetone reaction over HZSM-5.
4) Use as feedstock mixtures of ketones and alcohols similar to those obtained with real fermentation broth.
5) Hydrogenate the olefins obtained from isopropanol with different catalyst such as $Cu_2Cr_2O_5$ and Pd-carbon.
6) Modify the catalyst HZSM-5 with metals such Ni or Cu.

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APPENDIX A

COMPOUND ANALYSIS OF COMMERCIAL GASOLINES

Figures A1 to A8 show component analysis of commercial gasolines from a local Shell gas station taken in February 2009. Three types of gasoline were tested: regular, plus, and power. In the three types of gasoline, the most abundant component is C8, which increases as the gasoline grade improves. For example, the C8 concentration in regular gasoline is 20% whereas the concentration of C8 in power gasoline is 40%. In higher grades, the aromatics decrease and isoparaffins increase. The olefin concentration is less than 5%. In all gasoline types, the paraffin concentration is around 12%. In gasolines, the most abundant hydrocarbons are aromatics, paraffins, and isoparaffins.

Tables A1 to A5 show the most abundant components in gasoline, which accounts for 80 wt% of the total hydrocarbon in the mixture.

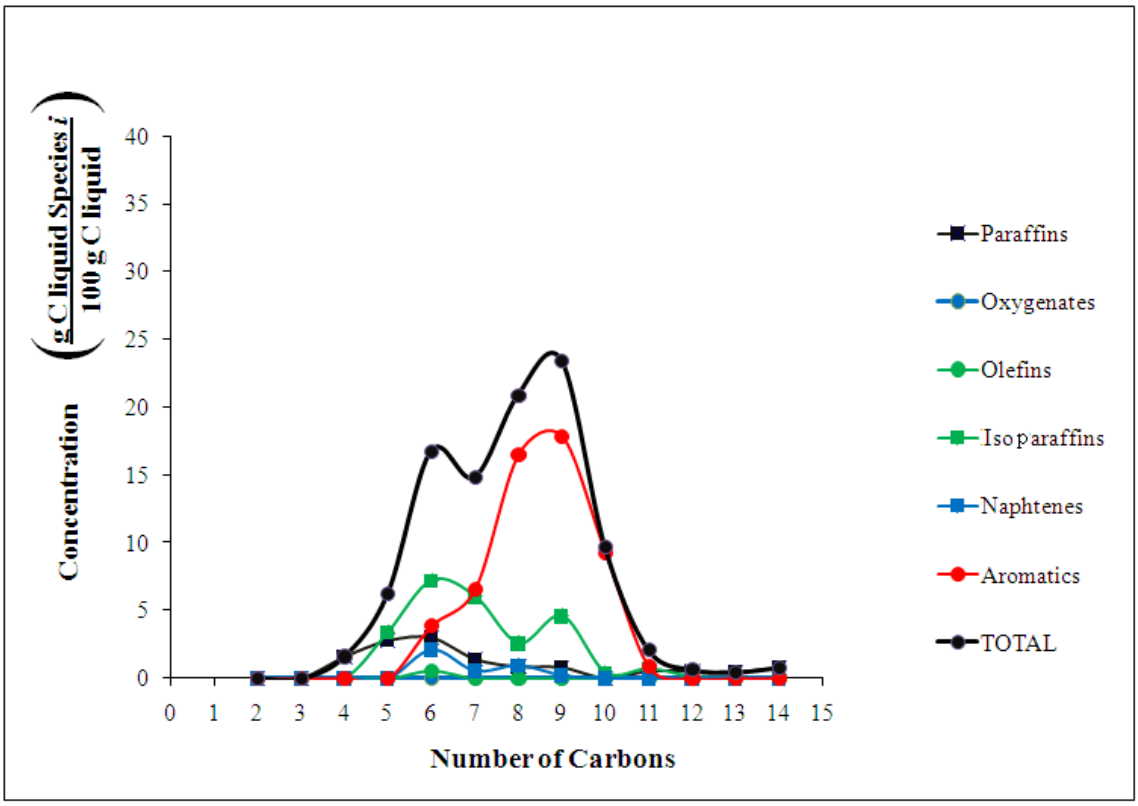

Figure A.1. Carbon distribution of commercial regular gasoline from a Shell gas station taken in February 2009.

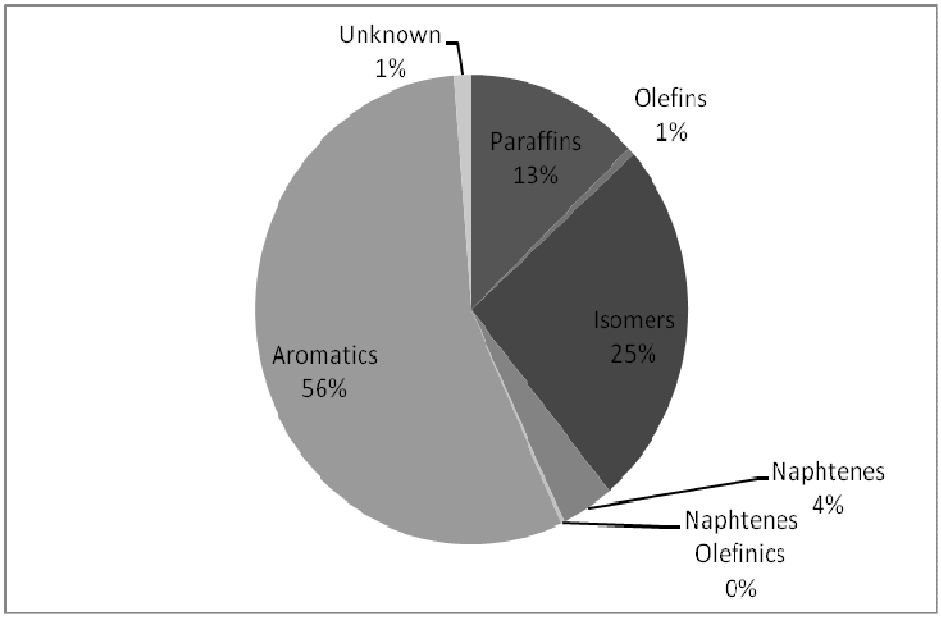

Figure A.2. Carbon distribution of commercial regular gasoline from a Shell gas station taken in February 2009.

Table A.1 Most abundant compounds in commercial regular gasoline from a Shell gas station taken in February 2009.

Paraffins (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)	
hexane	3.0	pentane, 2-methyl	3.8	benzene, 1,4-dimethyl	12.3
pentane	2.8	butane, 2-methyl	3.4	benzene, 1-ethyl-4-methyl	8.4
butane	1.6	butane, 2,2,3,3-tetramethyl	3.0	benzene, 1,2,3-trimethyl	7.3
heptane	1.4	pentane, 3-methyl	2.4	benzene, methyl	6.5
		hexane, 3-methyl	2.1	benzene	3.8
		octane, 4-methyl	1.6	benzene, ethyl	3.6
		pentane, 2,3,4-trimethyl	1.6	benzene, 1-methyl-3-(1-methylethyl)	3.0
		hexane, 2,4-dimethyl	1.5	benzene, 1-methyl-3-propyl	1.4
		butane, 2,2-dimethyl	0.8	benzene, 1,2,4,5-tetramethyl	0.9
				benzene, propyl	0.9

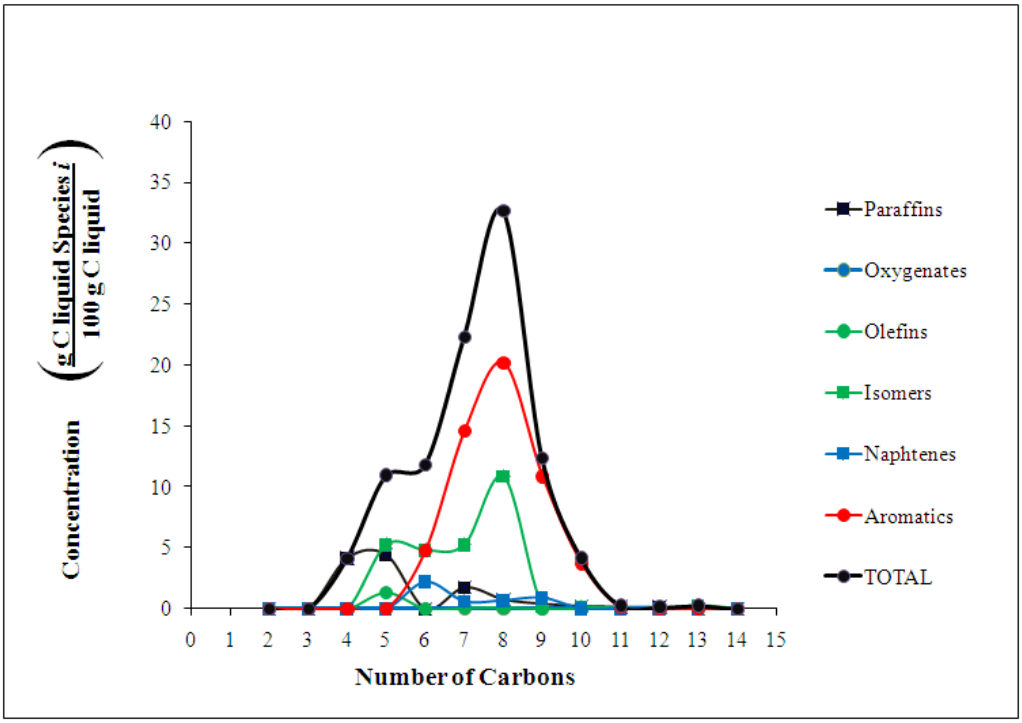

Figure A.3. Carbon distribution of commercial plus gasoline from a Shell gas station taken in February 2009.

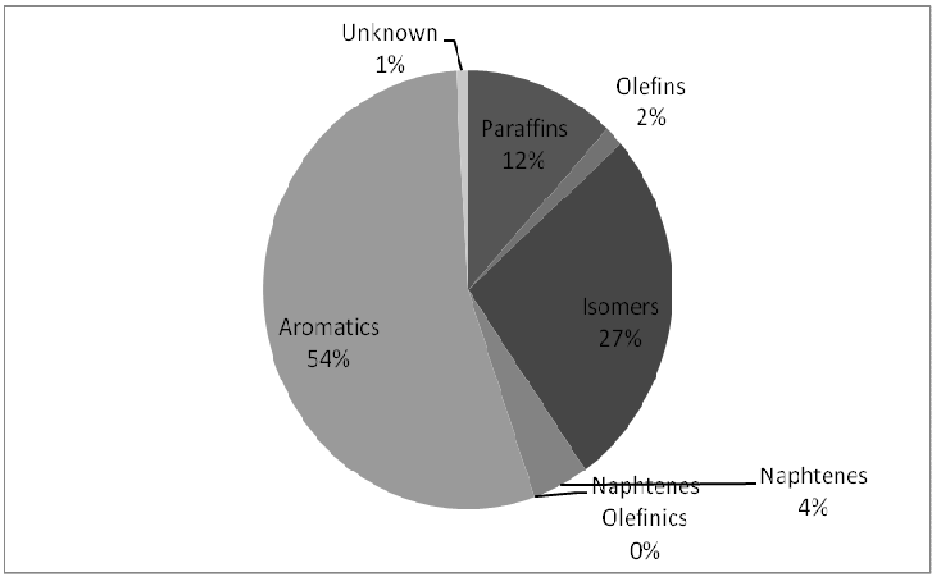

Figure A.4. Distribution of commercial plus gasoline from a Shell gas station taken in February 2009.

Table A.2 Most abundant compounds of a commercial plus gasoline from a Shell gas station taken in February 2009.

Paraffins (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)	
pentane	4.3	butane, 2-methyl	5.2	benzene, 1,3-dimethyl	16.5
butane	4.1	pentane, 2-methyl	4.8	benzene, methyl	14.5
		butane, 2,2,3,3-tetramethyl	4.4	benzene	4.7
		pentane, 3-methyl	2.8	benzene, ethyl	3.6
		pentane, 2,3,4-trimethyl	2.5	benzene, 1-ethyl-4-methyl	3.5
		heptane, 4-methyl	2.0	benzene, 1,3,5-trimethyl	3.4
		hexane, 3-methyl	1.8		
		hexane, 2,4-dimethyl	1.8		

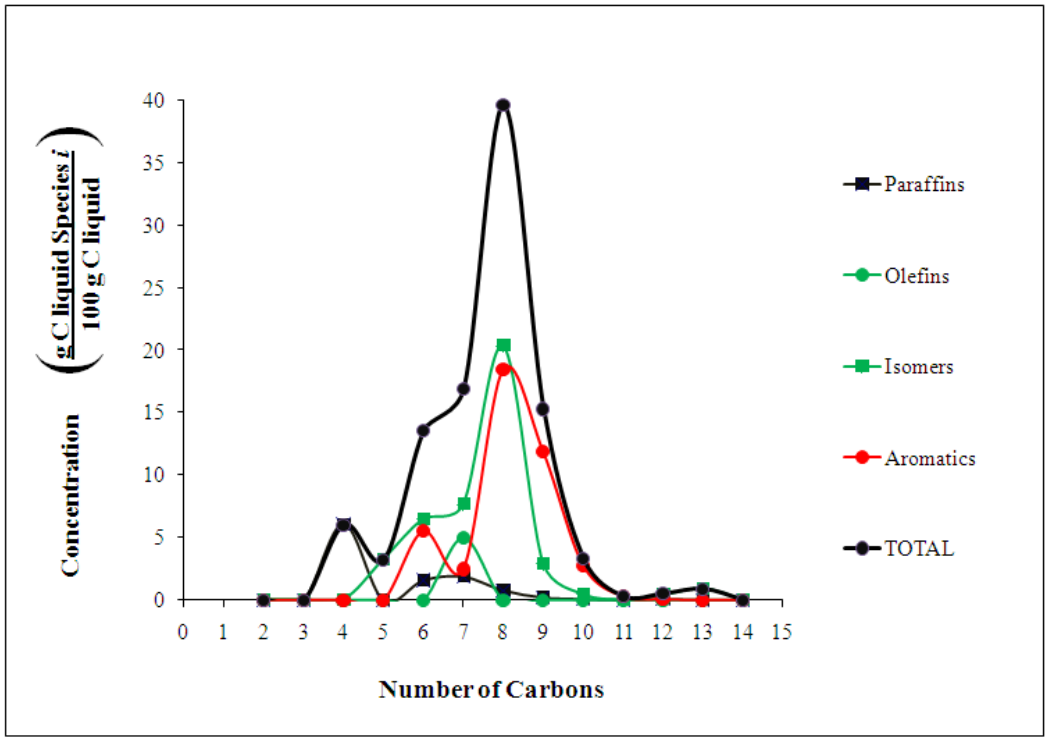

Figure A.5. Carbon distribution of commercial power gasoline from a Shell gas station taken in February 2009.

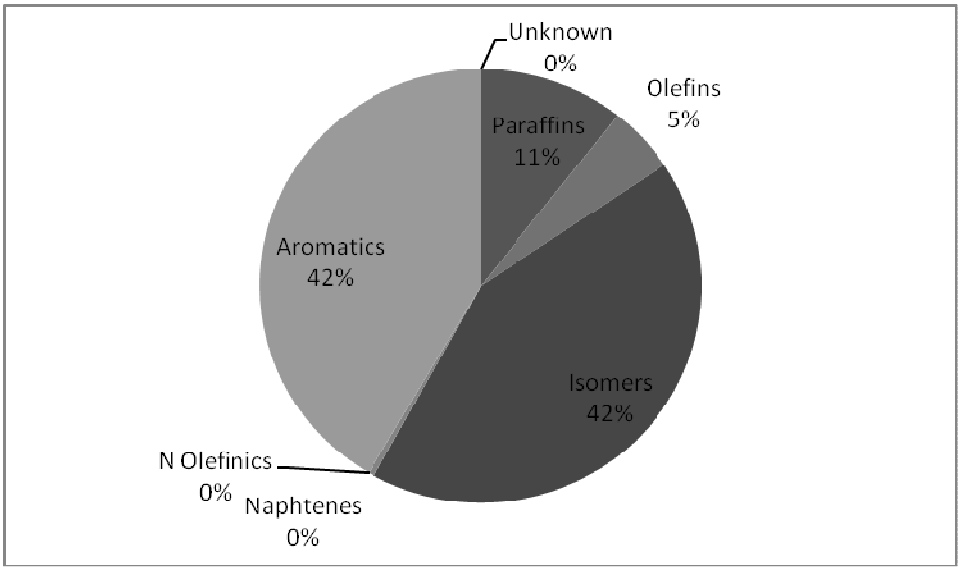

Figure A.6. Distribution of commercial power gasoline from a Shell gas station taken in February 2009.

Table A.3 Most abundant compounds of a commercial power gasoline from a Shell gas station taken in February 2009.

Paraffins (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)	
butane	5.7	pentane, 2,3,4-trimethyl	11.4	benzene, 1,4-dimethyl-	18.3
heptane	1.8	pentane, 2,2,4-trimethyl	8.9	benzene	5.5
		pentane, 2-methyl	5.0	benzene, 1,3,5-trimethyl-	4.0
		pentane, 2,4-dimethyl	5.0	benzene, 1-ethyl-4-methyl	3.6
		1,6-heptadiyne	4.8		
		butane, 2-methyl	3.2		
		pentano, 2,4-dimethyl	2.6		

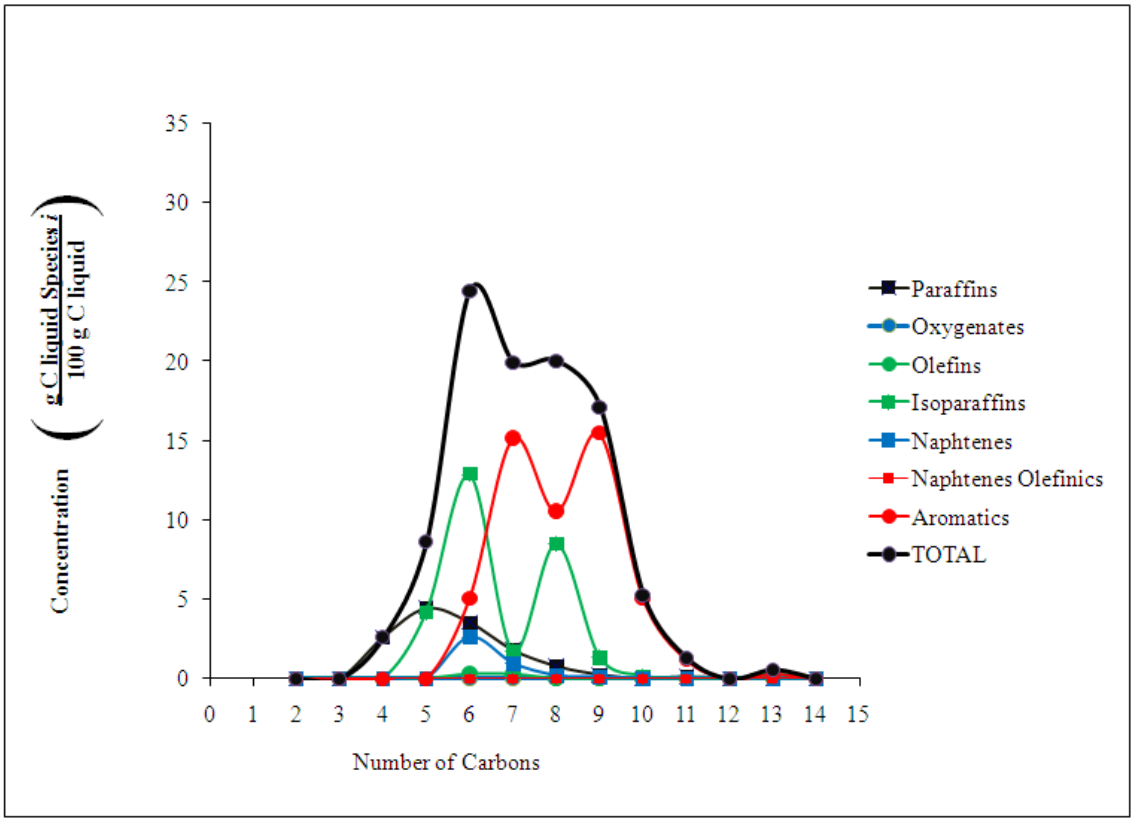

Figure A. 7 Carbon distribution of commercial plus gasoline from a Kroger gas station taken in October 2009.

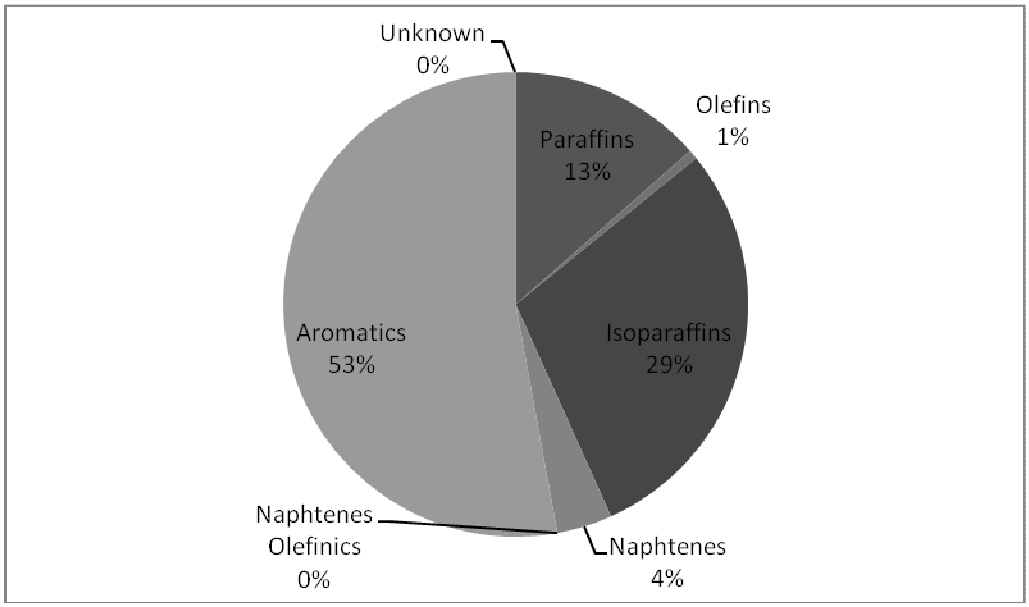

Figure A. 8 Distribution of commercial plus gasoline from a Kroger gas station taken in October 2009.

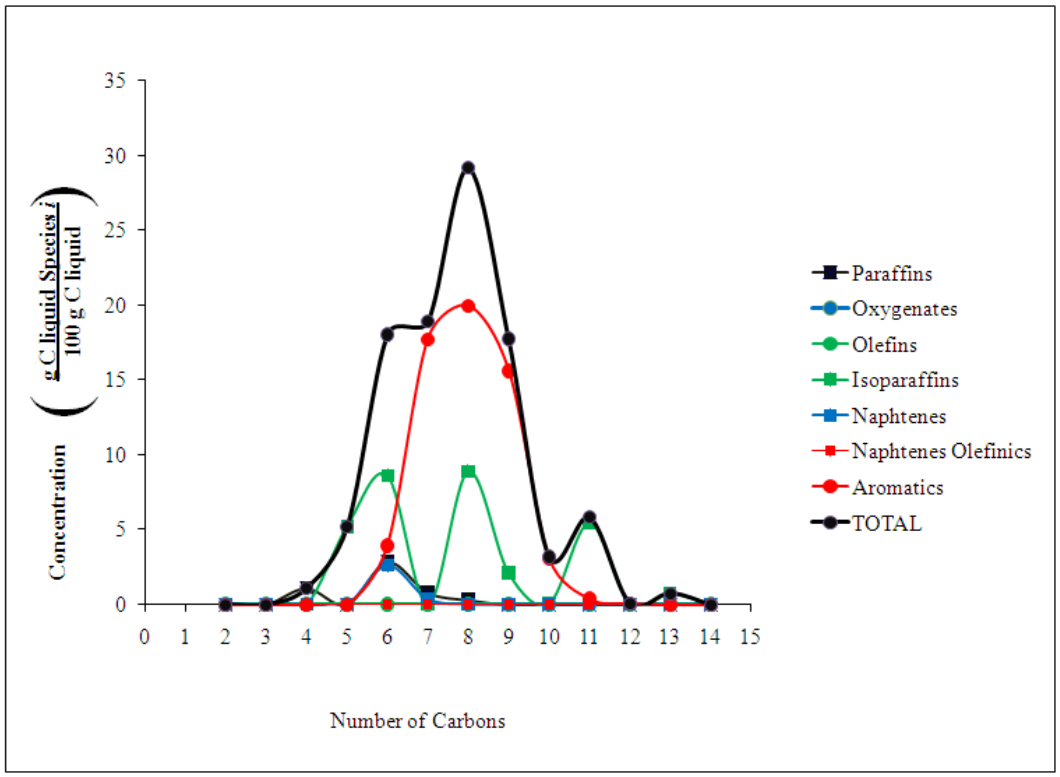

Figure A. 9 Carbon distribution of commercial power gasoline from a Kroger gas station taken in October 2009.

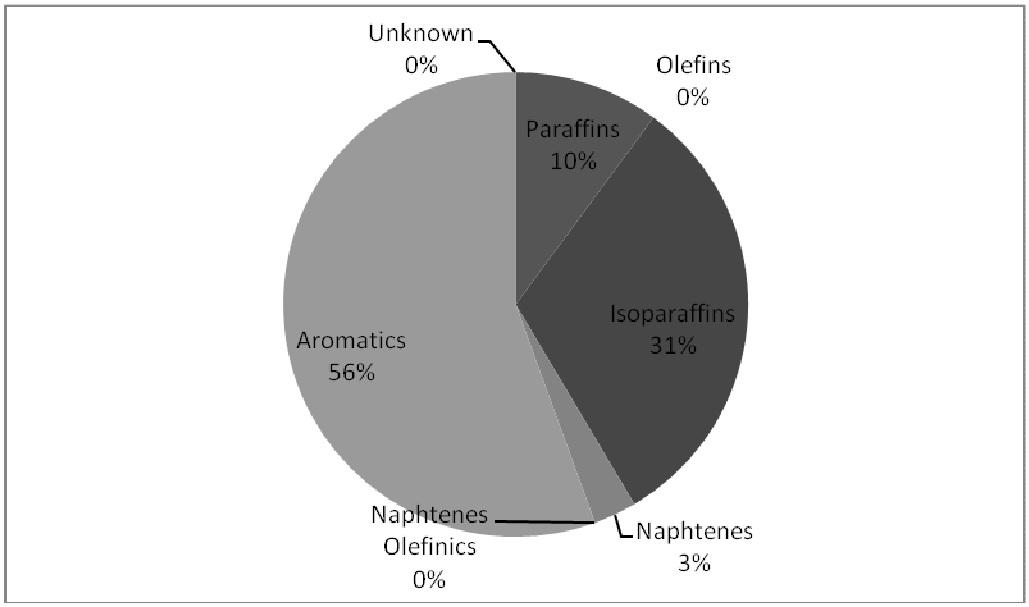

Figure A. 10 Distribution of commercial power gasoline from a Kroger gas station taken in October 2009.

APPENDIX B

TOTAL YIELD OF ISOPROPANOL REACTION OVER HZSM-5

This appendix presents mass balances for the isopropanol reactions. The basis for each table is 100 grams of isopropanol feed.

Table B.1 Product distribution for gases and liquids for isopropanol reaction (Experiment I1).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		300°C		1 atm		1.3 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	5.52	H_2O	30.38	
CO	0.00	C6	8.00	Isop.	0.00	
C1	0.07	**C6	0.00			
C2	0.14	C7	8.73			
*C2	1.08	C8	7.12			
C3	2.31	C9	5.24			
*C3	3.41	C10	2.50			
C4	14.00	C11	1.10			
*C4	7.90	C12	0.88			
		C13	0.91			
Total	28.91	+	40.01	+	30.38	99.30

*Olefin
** Benzene

Table B.2 Product distribution for gases and liquids for isopropanol reaction (Experiment I2).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		320°C		1 atm		1.3 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	1.93	H_2O	30.38	
CO	0.00	C6	6.18	Isop.	0.00	
C1	0.07	**C6	0.00			
C2	0.14	C7	10.55			
*C2	0.79	C8	10.71			
C3	1.48	C9	4.93			
*C3	5.24	C10	3.54			
C4	12.73	C11	1.09			
*C4	7.13	C12	1.20			
		C13	0.91			
Total	27.57	+	41.06	+	30.38	99.00

*Olefin
** Benzene

Table B.3 Product distribution for gases and liquids for isopropanol reaction (Experiment I3).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		370°C		1 atm		1.3 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	5.52	H_2O	30.38	
CO	0.00	C6	8.00	Isop.	0.00	
C1	0.07	**C6	0.00			
C2	0.14	C7	8.73			
*C2	1.08	C8	7.12			
C3	2.31	C9	5.24			
*C3	3.41	C10	2.50			
C4	14.00	C11	1.10			
*C4	7.90	C12	0.88			
		C13	0.91			
Total	28.91	+	40.01	+	30.38	99.30

Table B.4 Product distribution for gases and liquids for isopropanol reaction (Experiment I4).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		410°C		1 atm		1.3 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.19	C5	3.54	H_2O	30.16	
CO	0.00	C6	5.35	Isop.	0.00	
C1	0.14	**C6	0.00			
C2	0.28	C7	6.46			
*C2	2.06	C8	6.57			
C3	7.66	C9	3.86			
*C3	2.78	C10	1.82			
C4	16.54	C11	0.98			
*C4	8.32	C12	0.93			
		C13	0.92			
Total	37.98	+	30.43	+	30.16	98.57

*Olefin
** Benzene

Table B.5 Product distribution for gases and liquids for isopropanol reaction (Experiment I5).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		370°C		1 atm		0.52 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.18	C5	3.09	H_2O	30.16	
CO	0.02	C6	2.84	Isop.	0.00	
C1	0.09	**C6	0.00			
C2	0.19	C7	7.66			
*C2	1.94	C8	7.11			
C3	3.73	C9	8.78			
*C3	0.74	C10	4.87			
C4	14.34	C11	2.26			
*C4	8.61	C12	1.68			
		C13	0.92			
Total	29.84	+	39.20	+	30.16	99.21

Table B.6 Product distribution for gases and liquids for isopropanol reaction (Experiment I6).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		370°C		1 atm		1.9 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	5.52	H_2O	30.38	
CO	0.00	C6	8.00	Isop.	0.00	
C1	0.07	**C6	0.00			
C2	0.14	C7	8.73			
*C2	1.08	C8	7.12			
C3	2.31	C9	5.24			
*C3	3.41	C10	2.50			
C4	14.00	C11	1.10			
*C4	7.90	C12	0.88			
		C13	0.91			
Total	28.91	+	40.01	+	30.38	99.30

*Olefin
** Benzene

Table B.7 Product distribution for gases and liquids for isopropanol reaction (Experiment I7).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		370°C		1 atm		7.5 h^{-1}
		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	2.64	H_2O	30.24	
CO	0.00	C6	11.18	Isop.	0.00	
C1	0.07	**C6	0.28			
C2	0.14	C7	13.01			
*C2	0.87	C8	9.38			
C3	0.87	C9	2.76			
*C3	7.04	C10	1.69			
C4	9.46	C11	0.84			
*C4	6.79	C12	0.84			
		C13	0.91			
Total	25.23	+	43.54	+	30.24	99.01

Table B.8 Product distribution for gases and liquids for isopropanol reaction (Experiment I8).

Catalyst		***T***		***P***		**WHSV**
HZSM-5 (280)		370°C		1 atm		11.2 h^{-1}
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.00	C5	3.25	H_2O	30.38	
CO	0.00	C6	10.84	Isop.	0.00	
C1	0.07	**C6	0.00			
C2	0.14	C7	4.55			
*C2	0.55	C8	9.16			
C3	0.92	C9	4.18			
*C3	9.52	C10	2.40			
C4	12.07	C11	1.20			
*C4	8.71	C12	0.84			
		C13	0.91			
Total	31.99	+	37.34	+	30.38	99.70

*Olefin
** Benzene

APPENDIX C

TOTAL YIELD OF ACETONE REACTION OVER HZSM-5

A mass balance analysis of the acetone reaction experiments is presented. One hundred grams of acetone is chosen as a basis for the product distribution. The products are divided into gases and liquids. The liquid products are divided in hydrocarbons and aqueous products. The conditions for each experiment are shown before each result table. The type of catalysts for these experiments are HZSM-5 (80) and HZSM-5 (280)

Table C.1 Product distribution for gases and liquids for acetone reaction (Experiment A1).

Catalyst		***T***	***P***	**WHSV**		**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)		305°C	1 atm	1.3 h^{-1}		0
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	1.81	C5	1.26	H_2O	26.41	
CO	0.46	C6	2.33	Acetone	6.62	
C1	0.22	**C6	0.32			
C2	0.00	C7	5.78			
*C2	1.13	C8	8.85			
C3	0.82	C9	22.19			
*C3	0.96	C10	5.53			
C4	7.10	C11	1.63			
*C4	2.63	C12	1.99			
		C13	1.94			
Total	15.13	+	51.84	+	33.03	100.00

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Table C.2 Product distribution for gases and liquids for acetone reaction (Experiment A2).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	350°C	1 atm	1.3 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	16.23	C5	0.57	H_2O	14.61	
CO	2.60	C6	0.40	Acetone	5.59	
C1	0.35	**C6	0.92			
C2	0.58	C7	4.64			
*C2	2.30	C8	8.52			
C3	3.68	C9	10.25			
*C3	5.81	C10	3.52			
C4	9.63	C11	1.75			
*C4	5.66	C12	1.22			
		C13	1.16			
Total	46.85	+	32.95	+	20.20	100.00

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Table C.3 Product distribution for gases and liquids for acetone reaction (Experiment A3).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	350°C	1 atm	2.63 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.85	C5	0.28	H_2O	25.26	
CO	0.00	C6	1.62	Acetone	15.43	
C1	0.06	**C6	1.47			
C2	0.00	C7	7.73			
*C2	0.34	C8	11.16			
C3	0.17	C9	18.58			
*C3	0.32	C10	6.11			
C4	4.73	C11	2.98			
*C4	0.45	C12	1.23			
		C13	1.24			
Total	6.92	+	52.39	+	40.69	100.00

Table C.4 Product distribution for gases and liquids for acetone reaction (Experiment A4).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	350°C	1 atm	3.95 h^{-1}	0

		Liquid				
Gas		Hydrocarbons		Aqueous		
CO_2	2.48	C5	0.64	H_2O	21.15	
CO	0.51	C6	0.63	Acetone	18.32	
C1	0.12	**C6	0.71			
C2	0.00	C7	5.79			
*C2	0.66	C8	14.11			
C3	0.79	C9	19.11			
*C3	0.61	C10	6.24			
C4	2.06	C11	2.43			
*C4	1.38	C12	1.33			
		C13	0.92			
Total	8.61	+	51.92	+	39.47	100.00

Table C.5 Product distribution for gases and liquids for acetone reaction (Experiment A5). .

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	350°C	1 atm	5.30 h^{-1}	0

		Liquid				
Gas		Hydrocarbons		Aqueous		
CO_2	0.07	C5	0.51	H_2O	23.63	
CO	0.02	C6	1.24	Acetone	22.17	
C1	0.06	**C6	0.67			
C2	0.00	C7	6.38			
*C2	0.16	C8	11.57			
C3	0.20	C9	16.69			
*C3	0.21	C10	8.26			
C4	0.74	C11	3.76			
*C4	0.55	C12	1.90			
		C13	1.21			
Total	2.01	+	52.18	+	45.80	100.00

Table C.6 Product distribution for gases and liquids for acetone reaction (Experiment A6).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	1.3 h^{-1}	0

Gas		Liquid				
		Hydrocarbon		Aqueous		
CO_2	21.27	C5	0.47	H_2O	11.98	
CO	3.59	C6	0.00	Acetone	0.00	
C1	0.99	**C6	1.42			
C2	0.68	C7	3.47			
*C2	1.45	C8	7.62			
C3	3.33	C9	4.57			
*C3	15.88	C10	2.13			
C4	11.54	C11	1.18			
*C4	6.20	C12	1.14			
		C13	1.07			
Total	64.93	+	23.09	+	11.98	100.00

Table C.7 Product distribution for gases and liquids for acetone reaction (Experiment A7).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	1.3 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	13.58	C5	1.06	H_2O	19.31	
CO	1.74	C6	0.46	Acetone	0.00	
C1	1.00	**C6	2.07			
C2	0.58	C7	6.12			
*C2	0.88	C8	13.69			
C3	9.83	C9	9.76			
*C3	1.04	C10	3.64			
C4	6.29	C11	1.85			
*C4	4.00	C12	1.91			
		C13	1.19			
Total	38.95	+	41.74	+	19.31	100.00

Table C.8 Product distribution for gases and liquids for acetone reaction (Experiment A8).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	3.95 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	10.70	C5	0.30	H_2O	21.73	
CO	1.64	C6	0.39	Acetone	0.00	
C1	0.19	**C6	1.82			
C2	0.13	C7	8.29			
*C2	2.02	C8	15.87			
C3	3.53	C9	12.50			
*C3	3.31	C10	3.71			
C4	6.08	C11	1.68			
*C4	3.87	C12	1.13			
		C13	1.11			
Total	31.47	+	46.79	+	21.73	100.00

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Table C.9 Product distribution for gases and liquids for acetone reaction (Experiment A9).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	5.27 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	8.22	C5	1.26	H_2O	22.17	
CO	1.26	C6	1.15	Acetone	4.84	
C1	0.16	**C6	1.43			
C2	0.10	C7	8.46			
*C2	1.58	C8	15.03			
C3	2.75	C9	13.75			
*C3	2.59	C10	3.69			
C4	4.78	C11	1.57			
*C4	3.08	C12	1.19			
		C13	0.95			
Total	24.51	+	48.48	+	27.01	100.00

Table C.10 Product distribution for gases and liquids for acetone reaction (Experiment A10).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	6.58 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.85	C5	0.28	H_2O	25.27	
CO	0.00	C6	0.88	Acetone	15.43	
C1	0.06	**C6	1.53			
C2	0.00	C7	9.27			
*C2	0.34	C8	16.64			
C3	0.17	C9	16.33			
*C3	0.32	C10	3.60			
C4	4.73	C11	1.88			
*C4	0.45	C12	1.11			
		C13	0.86			
Total	6.92	+	52.38	+	40.70	100.00

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Table C.11 Product distribution for gases and liquids for acetone reaction (Experiment A11).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	7.9 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	9.01	C5	0.46	H_2O	19.51	
CO	0.71	C6	0.94	Acetone	11.25	
C1	0.14	**C6	0.85			
C2	0.00	C7	7.46			
*C2	2.09	C8	12.17			
C3	0.80	C9	16.18			
*C3	0.99	C10	4.23			
C4	6.04	C11	1.91			
*C4	3.10	C12	1.09			
		C13	1.07			
Total	22.87	+	46.36	+	30.77	100.00

Table C.12 Product distribution for gases and liquids for acetone reaction (Experiment A12).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	1.3 h^{-1}	0.34

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	13.00	C5	0.41	H_2O	19.86	
CO	1.78	C6	0.00	Acetone	0.00	
C1	0.52	**C6	2.34			
C2	0.43	C7	9.58			
*C2	0.78	C8	12.06			
C3	1.74	C9	8.86			
*C3	10.40	C10	3.04			
C4	6.44	C11	2.07			
*C4	4.04	C12	1.51			
		C13	1.16			
Total	39.12	+	41.02	+	19.86	100.00

Table C.13 Product distribution for gases and liquids for acetone reaction (Experiment A13).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	2.63 h^{-1}	0.34

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.67	C5	1.14	H_2O	30.30	
CO	0.39	C6	1.21	Acetone	0.00	
C1	0.05	**C6	2.82			
C2	0.00	C7	7.99			
*C2	0.13	C8	10.44			
C3	0.48	C9	27.17			
*C3	0.16	C10	7.96			
C4	0.64	C11	3.13			
*C4	0.92	C12	2.57			
		C13	1.81			
Total	3.45	+	66.25	+	30.30	100.00

Table C.14 Product distribution for gases and liquids for acetone reaction (Experiment A14).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	3.95 h^{-1}	0.34

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	2.22	C5	0.27	H_2O	29.36	
CO	0.23	C6	0.32	Acetone	0.00	
C1	0.08	**C6	2.30			
C2	0.00	C7	12.31			
*C2	0.56	C8	20.65			
C3	0.51	C9	16.35			
*C3	0.58	C10	4.63			
C4	2.46	C11	2.69			
*C4	1.52	C12	1.64			
		C13	1.33			
Total	8.16	+	62.49	+	29.36	100.00

Table C.15 Product distribution for gases and liquids for acetone reaction (Experiment A15).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	1.3 h^{-1}	1

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	6.66	C5	0.45	H_2O	25.55	
CO	0.91	C6	0.26	Acetone	0.00	
C1	0.26	**C6	2.16			
C2	0.26	C7	11.32			
*C2	0.71	C8	17.58			
C3	0.97	C9	11.96			
*C3	4.89	C10	4.29			
C4	3.62	C11	2.85			
*C4	2.38	C12	1.77			
		C13	1.14			
Total	20.67	+	53.79	+	25.55	100.00

Table C.16 Product distribution for gases and liquids for acetone reaction (Experiment A16).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (80)	415°C	1 atm	2.63 h^{-1}	1

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	6.52	C5	0.76	H_2O	25.69	
CO	0.86	C6	0.63	Acetone	0.00	
C1	0.18	**C6	2.38			
C2	0.13	C7	13.70			
*C2	1.41	C8	13.30			
C3	2.24	C9	17.09			
*C3	2.14	C10	3.44			
C4	4.20	C11	1.07			
*C4	2.83	C12	0.67			
		C13	0.73			
Total	20.52	+	53.78	+	25.69	100.00

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Table C.17 Product distribution for gases and liquids for acetone reaction (Experiment A17).

Catalyst	***T***	***P***	**WHSV**	**mol H_2 / mol Acetone**
HZSM-5 (80)	415°C	1 atm	3.95 h^{-1}	1

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	0.15	C5	0.59	H_2O	31.12	
CO	0.04	C6	0.66	Acetone	0.00	
C1	0.07	**C6	1.23			
C2	0.00	C7	11.62			
*C2	0.19	C8	21.52			
C3	0.21	C9	19.94			
*C3	0.22	C10	6.55			
C4	0.95	C11	1.71			
*C4	0.59	C12	1.37			
		C13	1.28			
Total	2.40	+	66.48	+	31.12	100.00

Table C.18 Product distribution for gases and liquids for acetone reaction (Experiment A18).

Catalyst		***T***	***P***	**WHSV**		**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)		415°C	1 atm	1.3 h^{-1}		0
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	4.45	C5	1.38	H_2O	27.47	
CO	0.47	C6	1.07	Acetone	0.00	
C1	0.23	**C6	1.73			
C2	0.20	C7	9.54			
*C2	1.04	C8	18.06			
C3	1.30	C9	15.04			
*C3	1.59	C10	6.70			
C4	2.48	C11	2.03			
*C4	1.80	C12	1.63			
		C13	1.79			
Total	13.55	+	58.97	+	27.47	100.00

Table C.19 Product distribution for gases and liquids for acetone reaction (Experiment A19).

Catalyst		***T***	***P***	**WHSV**		**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)		415°C	1 atm	2.63 h^{-1}		0
Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	6.62	C5	1.51	H_2O	25.46	
CO	0.73	C6	0.89	Acetone	0.00	
C1	0.14	**C6	1.39			
C2	0.24	C7	9.12			
*C2	1.83	C8	17.72			
C3	1.21	C9	14.13			
*C3	1.99	C10	3.87			
C4	4.71	C11	2.30			
*C4	3.51	C12	1.50			
		C13	1.11			
Total	20.99	+	53.55	+	25.46	100.00

Table C.20 Product distribution for gases and liquids for acetone reaction (Experiment A20).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	3.95 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	1.51	C5	0.66	H_2O	25.71	
CO	0.08	C6	1.02	Acetone	11.17	
C1	0.07	**C6	1.34			
C2	0.00	C7	8.58			
*C2	0.26	C8	17.31			
C3	0.26	C9	19.45			
*C3	0.39	C10	4.20			
C4	2.71	C11	2.14			
*C4	0.92	C12	1.25			
		C13	0.97			
Total	6.20	+	56.92	+	36.88	100.00

Table C.21 Product distribution for gases and liquids for acetone reaction (Experiment A21).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	5.97 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	3.36	C5	0.52	H_2O	24.11	
CO	0.25	C6	1.98	Acetone	10.31	
C1	0.09	**C6	1.14			
C2	0.00	C7	7.84			
*C2	0.70	C8	11.03			
C3	0.44	C9	21.87			
*C3	1.54	C10	4.85			
C4	4.01	C11	2.29			
*C4	1.82	C12	1.00			
		C13	0.85			
Total	12.21	+	53.37	+	34.42	100.00

Table C.22 Product distribution for gases and liquids for acetone reaction (Experiment A24).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	1.3 h^{-1}	0.5

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	7.41	C5	0.66	H_2O	24.26	
CO	0.80	C6	0.84	Acetone	0.00	
C1	0.30	**C6	1.01			
C2	0.07	C7	8.65			
*C2	1.81	C8	17.97			
C3	1.57	C9	17.17			
*C3	2.13	C10	5.22			
C4	3.08	C11	1.50			
*C4	2.83	C12	1.50			
		C13	1.25			
Total	19.99	+	55.75	+	24.26	100.00

Table C.23 Product distribution for gases and liquids for acetone reaction (Experiment A25).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	2.63 h^{-1}	0.5

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	5.98	C5	0.78	H_2O	25.55	
CO	0.54	C6	0.99	Acetone	0.00	
C1	0.24	**C6	0.89			
C2	0.00	C7	8.56			
*C2	1.40	C8	14.26			
C3	0.85	C9	17.16			
*C3	2.01	C10	7.09			
C4	4.58	C11	1.67			
*C4	3.17	C12	3.26			
		C13	1.02			
Total	18.77	+	55.68	+	25.55	100.00

Table C.24 Product distribution for gases and liquids for acetone reaction (Experiment A27).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	1.3 h^{-1}	1

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	7.07	C5	1.04	H_2O	25.01	
CO	0.82	C6	1.28	Acetone	0.00	
C1	0.34	**C6	1.58			
C2	0.09	C7	10.08			
*C2	1.46	C8	15.24			
C3	1.88	C9	14.23			
*C3	2.14	C10	5.97			
C4	3.55	C11	2.90			
*C4	2.54	C12	1.31			
		C13	1.45			
Total	19.90	+	55.09	+	25.01	100.00

Table C.25 Product distribution for gases and liquids for acetone reaction (Experiment A23).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	1 atm	1.3 h^{-1}	0.34

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	1.20	C5	1.06	H_2O	30.17	
CO	0.38	C6	1.51	Acetone	0.00	
C1	0.56	**C6	1.69			
C2	0.17	C7	9.82			
*C2	2.30	C8	13.07			
C3	3.82	C9	9.94			
*C3	4.38	C10	6.54			
C4	5.41	C11	1.61			
*C4	3.77	C12	1.31			
		C13	1.31			
Total	21.97	+	47.86	+	30.17	100.00

Table C.26 Product distribution for gases and liquids for acetone reaction (Experiment A30).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	1.3 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	11.57	C5	0.30	H_2O	20.72	
CO	2.12	C6	0.17	Acetone	0.00	
C1	1.61	**C6	2.18			
C2	0.61	C7	10.21			
*C2	0.42	C8	11.15			
C3	1.23	C9	14.93			
*C3	0.77	C10	5.29			
C4	6.70	C11	2.07			
*C4	4.42	C12	1.94			
		C13	1.58			
Total	29.46	+	49.81	+	20.72	100.00

Table C.27 Product distribution for gases and liquids for acetone reaction (Experiment A31).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	3.95 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	11.59	C5	0.71	H_2O	18.36	
CO	2.40	C6	0.70	Acetone	5.71	
C1	0.70	**C6	0.87			
C2	0.17	C7	5.99			
*C2	1.16	C8	12.26			
C3	3.18	C9	16.28			
*C3	0.91	C10	5.31			
C4	5.55	C11	2.05			
*C4	3.25	C12	1.57			
		C13	1.28			
Total	28.92	+	47.02	+	24.07	100.00

Table C.28 Product distribution for gases and liquids for acetone reaction (Experiment A32).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	5.53 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	4.19	C5	3.24	H_2O	24.76	
CO	0.34	C6	1.67	Acetone	7.75	
C1	0.11	**C6	0.64			
C2	0.00	C7	6.17			
*C2	0.47	C8	8.70			
C3	0.28	C9	17.38			
*C3	0.88	C10	7.69			
C4	9.17	C11	2.55			
*C4	1.46	C12	1.12			
		C13	1.42			
Total	16.92	+	50.57	+	32.52	100.00

Table C.29 Product distribution for gases and liquids for acetone reaction (Experiment A32).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	5.53 h^{-1}	0

Gas		Liquid				
		Hydrocarbon		Aqueous		
CO_2	6.23	C5	1.50	H_2O	21.31	
CO	0.42	C6	2.00	Acetone	13.29	
C1	0.14	**C6	0.90			
C2	0.17	C7	4.77			
*C2	0.95	C8	9.19			
C3	0.30	C9	12.62			
*C3	1.24	C10	4.36			
C4	13.21	C11	1.31			
*C4	3.04	C12	1.47			
		C13	1.58			
Total	25.69	+	39.70	+	34.60	100.00

Table C.30 Product distribution for gases and liquids for acetone reaction (Experiment A33).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	9.48 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	1.70	C5	1.78	H_2O	22.19	
CO	0.17	C6	2.20	Acetone	21.72	
C1	0.08	**C6	0.84			
C2	0.00	C7	5.57			
*C2	0.27	C8	8.84			
C3	0.26	C9	16.13			
*C3	0.60	C10	6.50			
C4	4.45	C11	1.57			
*C4	1.41	C12	2.72			
		C13	0.99			
Total	8.95	+	47.13	+	43.92	100.00

*Olefin

** Benzene

Table C.31 Product distribution for gases and liquids for acetone reaction (Experiment A34).

Catalyst	***T***	***P***	**WHSV**	**H_2 Ratio (mol H_2 / mol acetone)**
HZSM-5 (280)	415°C	6.8 atm	11.85 h^{-1}	0

Gas		Liquid				
		Hydrocarbons		Aqueous		
CO_2	2.52	C5	0.45	H_2O	17.06	
CO	0.00	C6	0.87	Acetone	34.69	
C1	0.06	**C6	1.04			
C2	0.00	C7	4.29			
*C2	0.13	C8	7.39			
C3	0.19	C9	12.70			
*C3	0.19	C10	4.84			
C4	8.52	C11	1.55			
*C4	0.85	C12	1.33			
		C13	1.32			
Total	12.46	+	35.78	+	51.75	100.00

APPENDIX D

TYPE OF HYDROCARBON LIQUID PRODUCTS FROM THE ISOPROPANOL REACTION OVER HZSM-5

Table D.1 shows the most abundant type of liquid-phase hydrocarbons for the isopropanol reaction over HZSM-5.

Table D.2 shows the most abundant liquid-phase carbon compounds for the isopropanol reaction over HZSM-5.

Table D.1 Most abundant type of liquid-phase hydrocarbons for the isopropanol reaction

Catalyst: HZSM-5 (280)					
	WHSV (h^{-1})				
T (°C)	0.5	1.3	3.7	7.5	11
300		O			
320		O			
370	A	O	N	O	O
410		O			

A = Aromatics

O = Olefins

N = Naphtenes

Table D.2 Most abundant type of liquid-phase carbon compounds for the isopropanol reaction

Catalyst: HZSM-5 (280)					
WHSV (h^{-1})					
T (°C)	0.5	1.3	3.7	7.5	11
300		C7			
320		C7– C8			
370	C9	C8	C8	C8	C7
410		C7–C8			

Tables D.3 to D.10 and Figures D.1 to D.14 show the following:

1. Distribution of types of hydrocarbons at different carbon number
2. Total distribution of types of hydrocarbons
3. Most abundant compounds (represent 80% of the total concentration)

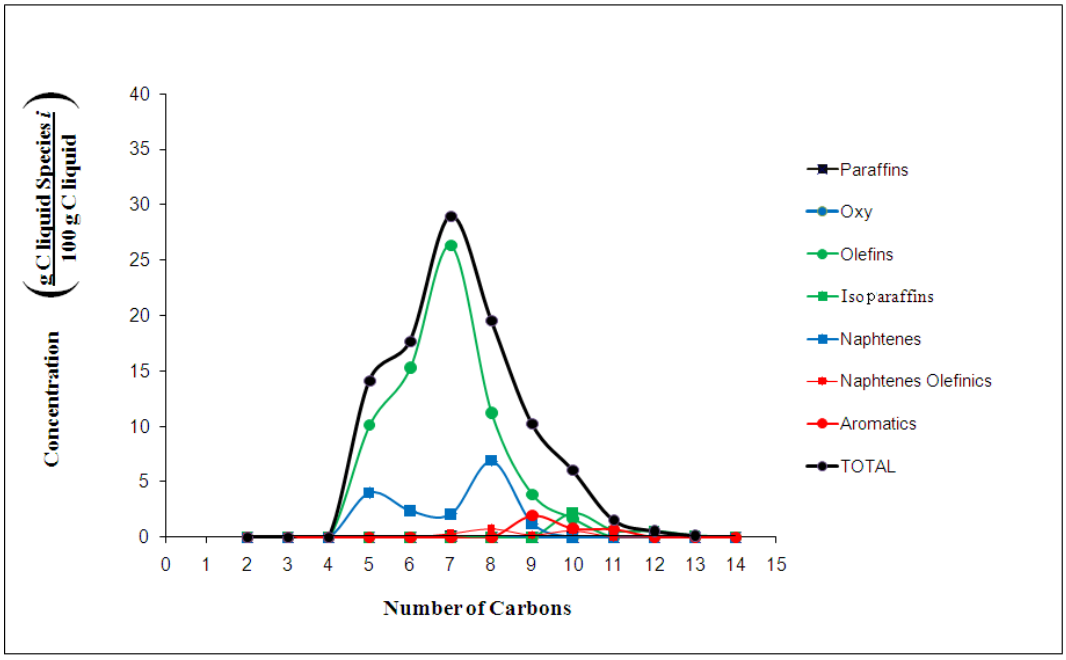

Figure D.1. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

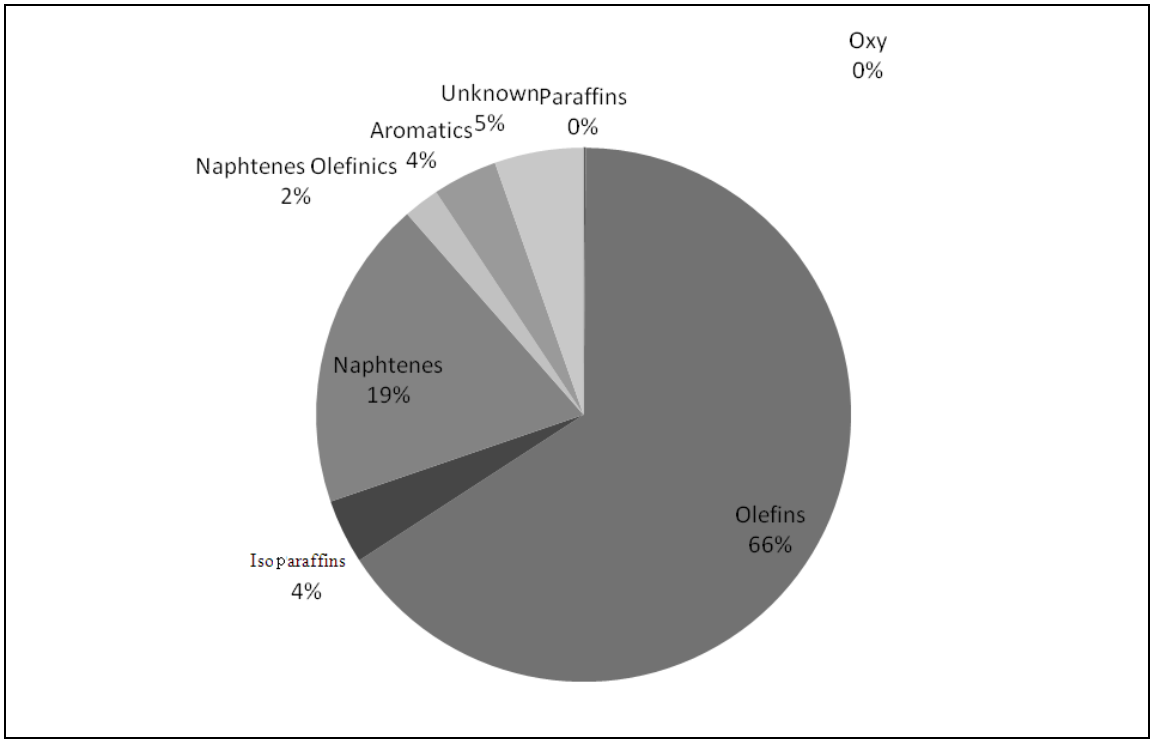

Figure D.2. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

Table D.3 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

Olefins (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)	
2-hexene, 2-methyl	9.4	cyclopropane, 1,1,2-trimethyl	4.0	benzene, 1-ethyl-2-methyl	1.0
2-pentene, 3-methyl	8.4	cyclohexane	2.3		
2-pentene	10.0	cyclobutane, isopropyliden	2.1		
2-hexene, 2,5-dimethyl	5.0	cyclohexane, 1-methyl-4-methylene	2.0		
2-pentene, 2,4-dimethyl	4.4	cyclopentane, 1,2-dimethyl-3-methylen	1.9		
2-pentene, 2-methyl	4.2	cyclopentane, 1-ethyl-3-methyl-cis	1.7		
3-heptene	3.8	cyclopropane, 1-methyl-2-pentyl	1.0		
2-heptene	3.6				
1-pentene, 2,3-dimethyl	2.9				
2-pentene, 2-methyl	2.5				
2-pentene, 3,4-dimethyl	1.9				
2-hexene, 2,3-dimethyl	1.8				
2-octene	1.7				
3-octene, 2,6-dimethyl	0.9				

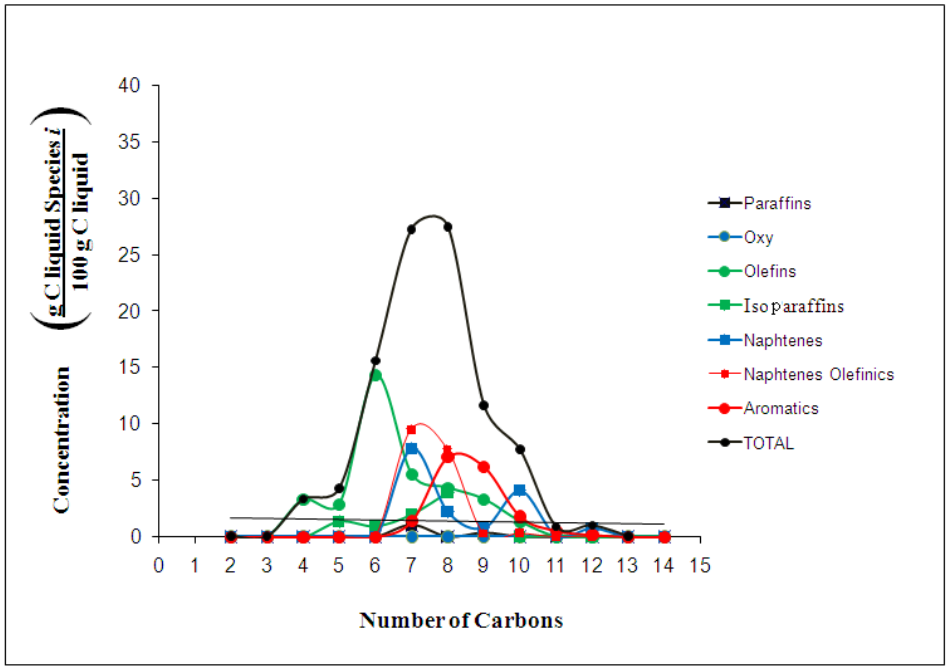

Figure D.3. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 320°C.

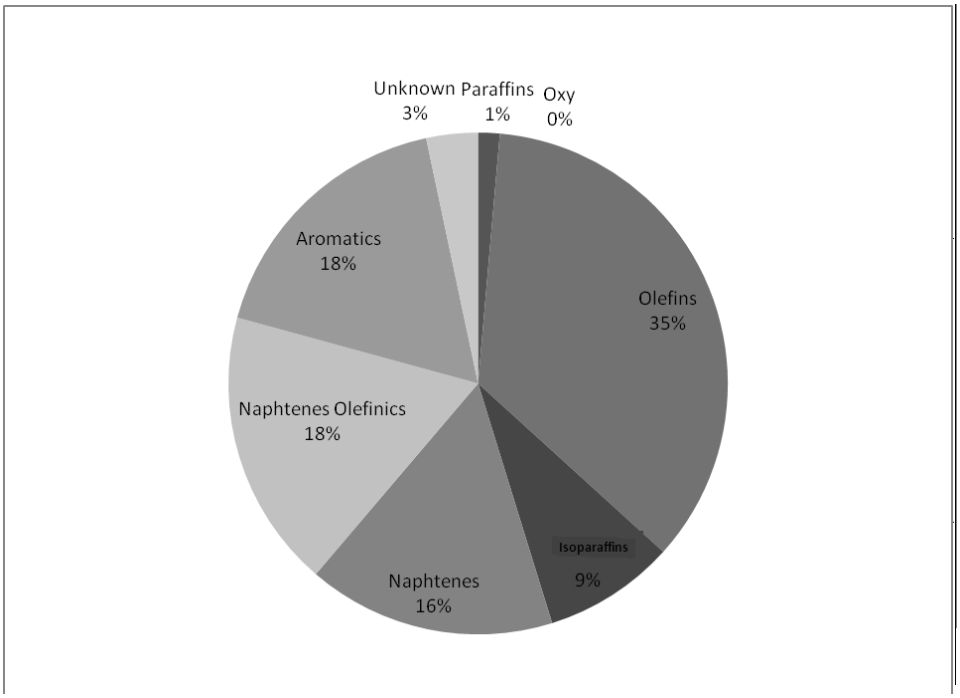

Figure D.4. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 320°C.

Table D.4 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 320°C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
2-butene, 2,3-dimethy	6.5	cyclopropane, 1,2-dimethyl	7.8	benzene, 1,3-dimethyl	4.8	hexane, 2-methyl	2.1
2,4-hexadiene, 2-methyl	4.0	cyclopentane, methylene	2.2	benzene, 1-ethyl-4-methyl	2.0	pentane, 2,4-dimethyl-2-nitro	1.9
2-butene	3.1	cyclopentane, 1,2-dimethyl-3-methylen	1.7	benzene, 1,3,5-trimethyl	1.9	butane, 2-methyl	1.3
1-butene, 2-methyl	2.9			benzene, methyl	1.4	hexane, 3-methyl	1.2
2-pentene, 4-methyl	2.7			diethyI benzene	1.3	pentane, 3-methyl	0.9
2-pentene, 3-methyl	2.3			benzene, 1-methyl-3-propyl	1.1		
1,4-pentadiene, 2,3,3-trimethyl	2.0			benzene, 1,2-dimethyl	0.8		
2-butene, 2,3-dimethyl	1.5			benzene, 1-methyl-2-(1-methylethyl)	0.8		
1,6-octadiene, 2,5-dimethyl	1.1						
1-pentene, 2-methyl	1.1						
cyclopentene, 4,4-dimethyl	4.6						
cyclohexene, 1,3-dimethyl	3.6						
cyclohexene, 1-methyl	3.0						
cyclohexene, 1,3-dimethyl	1.9						
cyclopentene, 1,5-dimethyl	1.7						

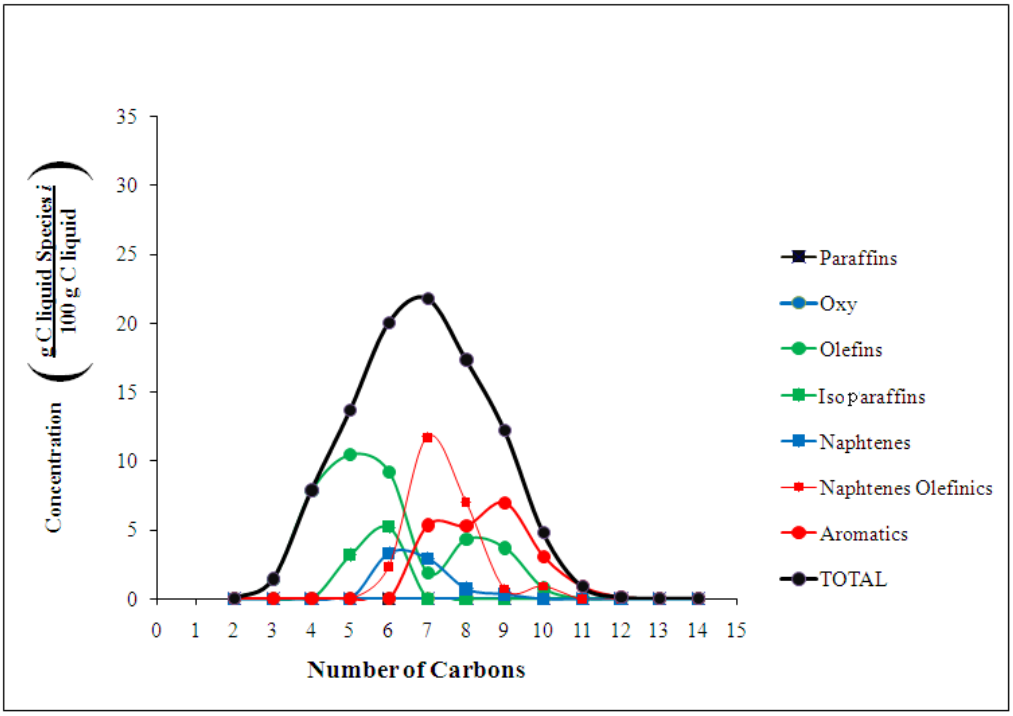

Figure D.5. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

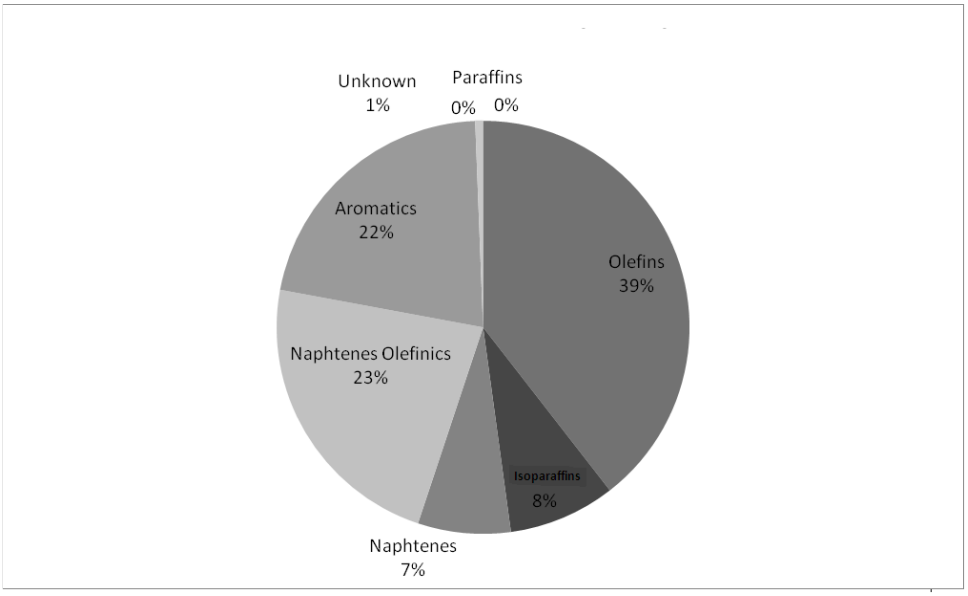

Figure D.6. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

Table D.5 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 370°C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
2-butene	7.8	1,2-dimethyl-cyclopentane,trans	2.4	xylene	4.0	2-methyl-pentane	4.1
2,3-dimethyl-1-butene	6.8	methyl-cyclopentane	2.3	1-ethyl, 4-methyl, benzene	3.7	2-methyl-butane	3.2
2-methyl-1-butene	5.3	cylcohexane	1.0	mesitylene	1.8	2-methyl-hexane	2.0
2-pentene	5.1			Toluene	1.6	3-methyl-hexane	1.2
3-methyl-2-pentene	2.3			ethyl benzene	1.2	3-methyl-pentane	1.0
1-propene	1.3						
2,5-dimethyl-2,4-hexadiene	1.3						
7-methyl-3-octyne	1.0						
2,3,3-trimethyl-1,4-pentadiene	1.0						
1,3-dimethyl-cyclopentene	4.9						
1,3-dimethyl-cyclohexene	2.8						
1,5-dimethyl-cyclopentene	2.7						
methylene-cyclopentane	2.3						
1,3-dimethyl-cyclohexene	1.9						
1-methyl-cyclohexene	1.7						
1,5-dimethyl-cyclopentene	1.4						

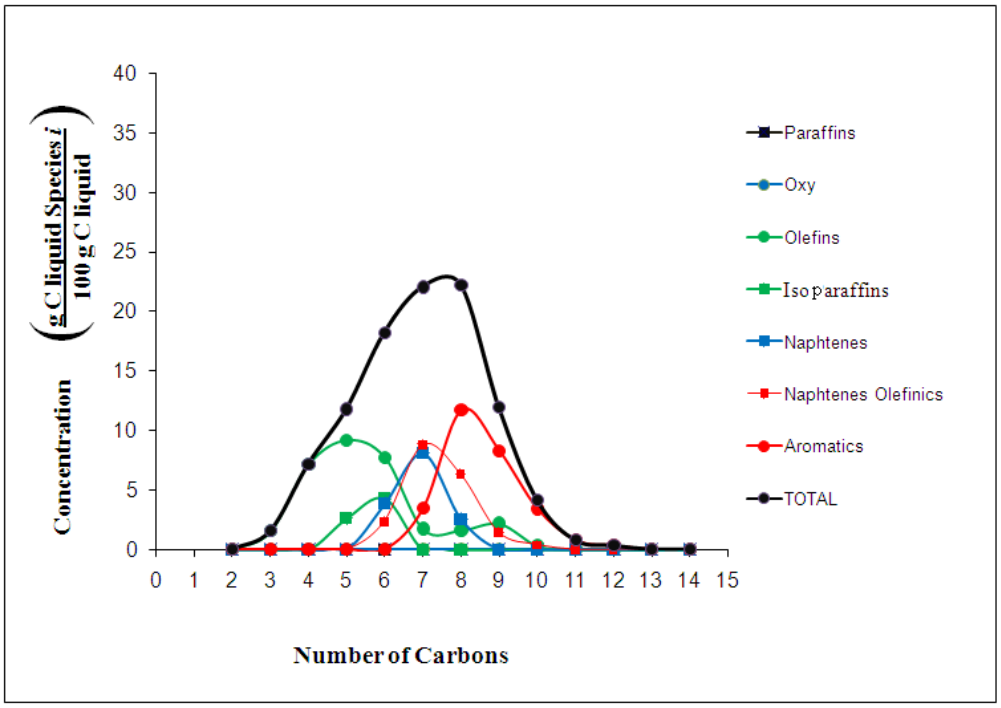

Figure D.7. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 410°C.

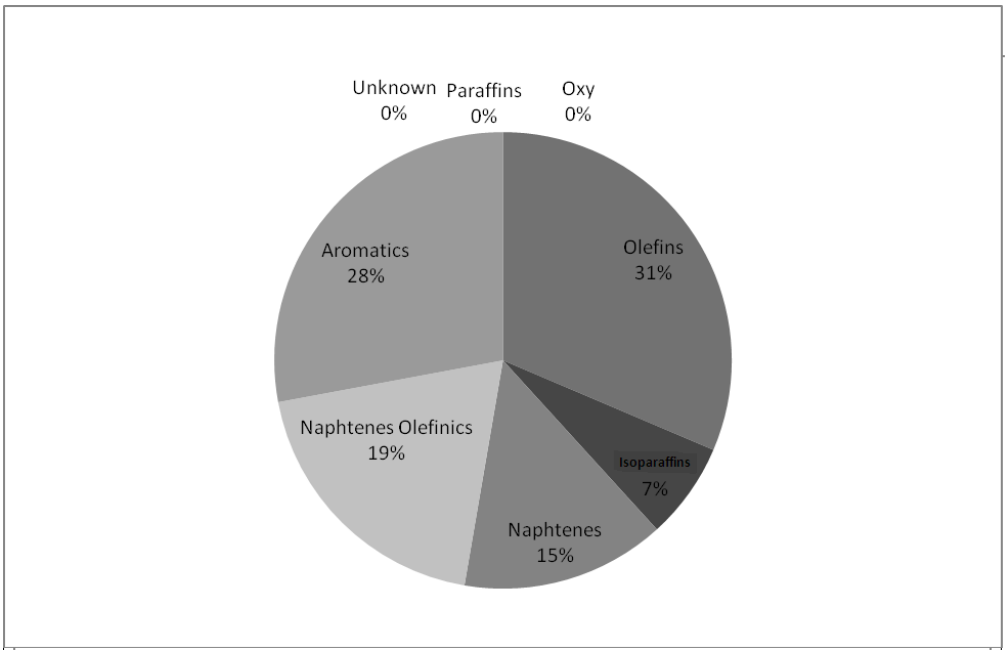

Figure D.8. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 410 °C.

Table D.6 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 1.3 h^{-1}, P = 1 atm (absolute), T = 410 °C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
2-butene	7.1	1,3-dimethyl-cyclopentane,cis	3.4	xylene	7.8	2-methyl-pentane	3.4
3-methyl-2-pentene, trans	5.8	methyl-cyclopentane	2.9	1-ethyl-2-methyl-benzene	4.9	2-methyl-butane	2.6
2-methyl-2-butene	4.7	2-methyl-hexane	1.9	toluene	3.4		
2-pentene	4.5	1,3-dimethyl-cylcohexane	1.5	mesitylene	2.7		
3-methyl-2-pentene, cis	2.0	1,1-dimethyl-cyclopentane	1.1	ethyl benzene	2.1		
1-propene	1.5			xylene	1.8		
3-methyl-1-hexene	1.2						
4,4-dimethyl-cyclopentene	4.3						
4,4-dimethyl-cyclopentene	2.9						
1,3-dimethyl-cyclohexene	2.7						
1-methyl-cyclopentene	2.4						
1,5-dimethyl-cyclopentene	1.3						
1,2-dimethyl-3-methylene-cyclopentane	1.2						

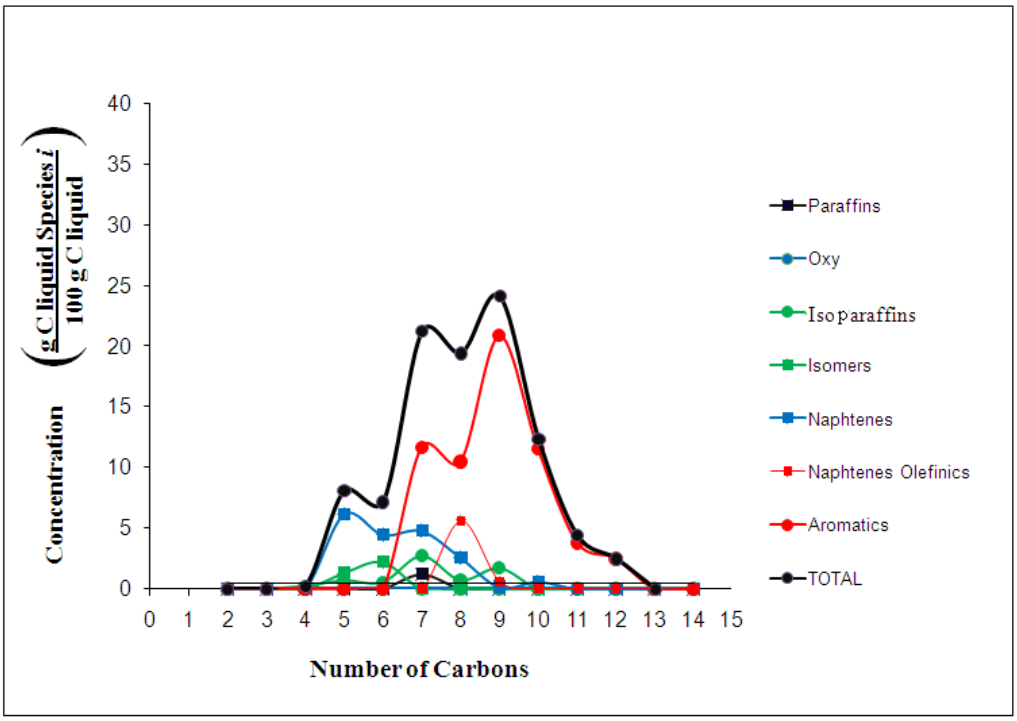

Figure D.9. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 0.52 h^{-1}, P = 1 atm (absolute), T = 370°C.

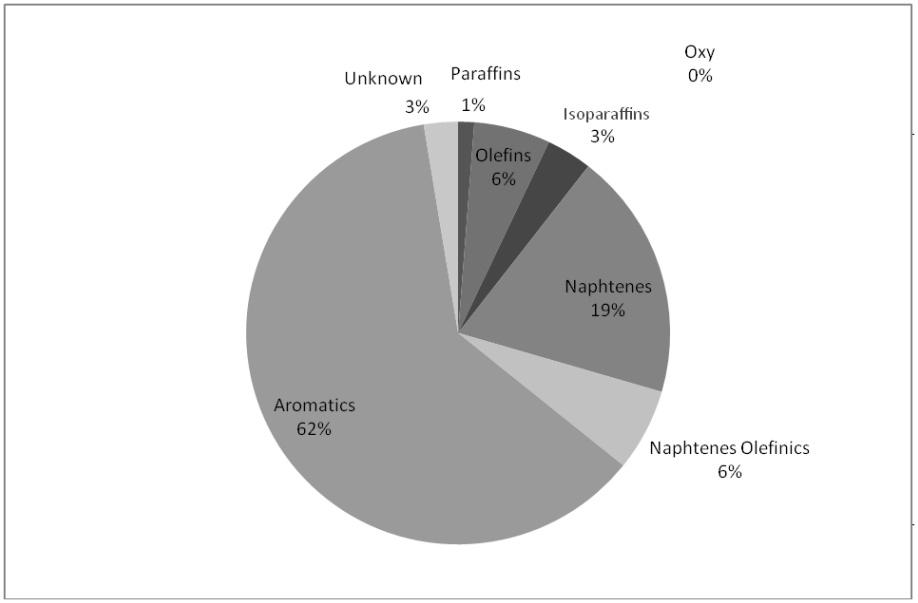

Figure D.10. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 0.52 h^{-1}, P = 1atm (absolute), T = 370°C.

Table D.7 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 0.52 h^{-1}, P = 1 atm (absolute), T = 370°C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
2,4-heptadiene	2.7	cyclopropane, 1,2-dimethyl	3.4	benzene, 1-ethyl-3-methyl	11.8	pentane, 3-methylene	2.1
3-octyne, 7-methyl	1.4	cyclopentane, methyl	3.0	benzene, methyl	10.2	hexane, 2-methyl	1.4
cyclohexene, 1,3-dimethyl		cyclopropane, 1,2-dimethyl	2.7	benzene, 1,2,3-trimethyl	7.4	butane, 2-methyl	1.2
		cyclopentane, 1,3-dimethyl	1.9	benzene, 1,3-dimethyl	5.4		
		cyclopentane, 1,3-dimethyl	1.8	benzene, (1-methylpropyl)	4.3		
		cyclopentane, 1,2-dimethyl -3-methylene	1.4	xylene	4.0		
		cyclopropane, (1-methylethenyl)	1.3	benzene, 1-methyl-4-(1-methylethyl)	2.6		
				p-mentha-1,5,8-triene	1.5		
				benzene, (1,1-dimethylpropyl)-	1.2		
				benzene, 1,3,5-trimethyl	1.0		

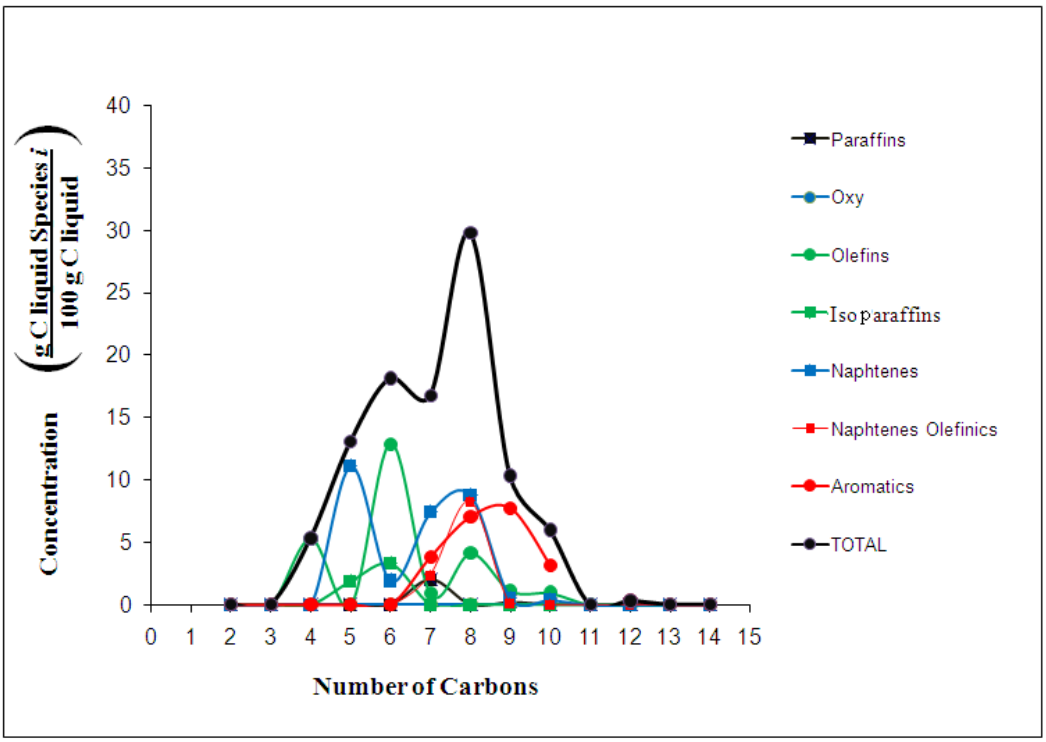

Figure D.11. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 3.7 h^{-1}, P = 1 atm (absolute), T = 370 °C.

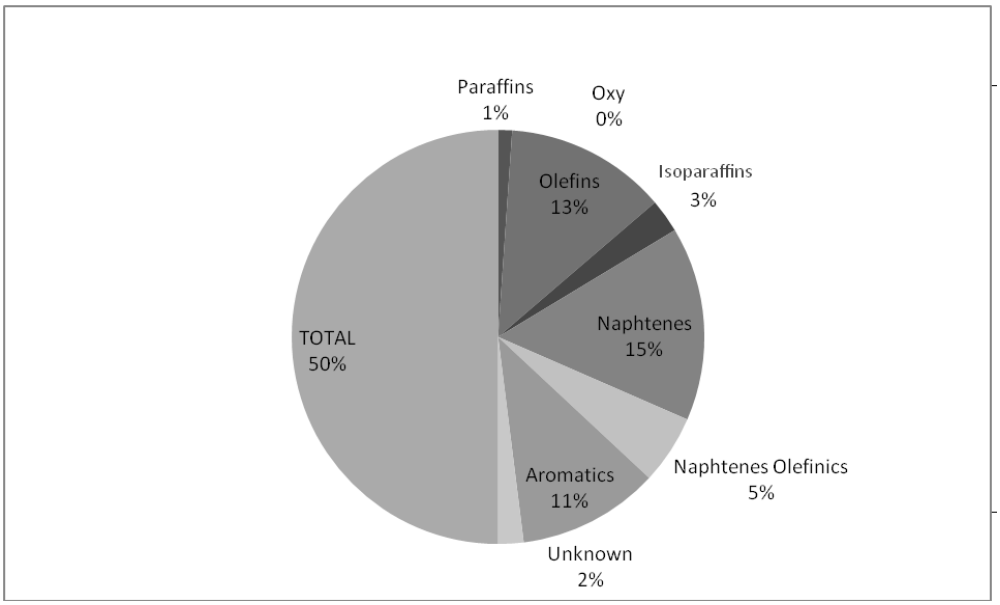

Figure D.12. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 3.7 h^{-1}, P = 1 atm (absolute), T = 370 °C.

Table D.8 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 3.7 h^{-1}, P = 1 atm (absolute), T = 370 °C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
1-butene, 2,3-dimethyl	6.6	cyclopropane, 1,2-dimethyl	7.5	benzene, 1,3-dimethyl	4.6	pentane, 2-methyl	3.3
1-propene, 2-methyl	5.3	cyclopentene, 4,4-dimethyl	4.2	benzene, 1-ethyl-2-methyl	4.3	hexane, 2-methyl	2.0
2-pentene, 3-methyl	2.2	cyclopropane, 1,2-dimethyl	3.6	benzene, 1,3,5-trimethyl	2.3	butane, 2-methyl	1.9
2-butene, 2,3-dimethyl	2.0	cyclopentene, 1,5-dimethyl	3.1	benzene, methyl	1.7		
1,4-pentadiene, 2,3,3-trimethyl	1.7	cyclopentane, 1,3-dimethyl	2.6	benzene, 1,2-diethyl	1.0		
1-pentene, 2-methyl	1.7	cyclopropane, (1-methylethenyl)	1.9	benzene, 1-methyl-3-propyl	1.0		
cyclohexene, 1,3-dimethyl	2.9	cyclopentane, 1,2-dimethyl-3-methylen	1.2	benzene, 1,4-dimethyl	0.9		
cyclohexene, 1-methyl	1.8	cyclohexane, 1-methyl-4-methylene	1.0				
cyclopentene, 1,5-dimethyl	1.4	cyclopentane, 1-ethyl-3-methyl	0.9				
cyclohexene, 1,3-dimethyl	1.4						
cyclohexene, 4-methyl	0.9						

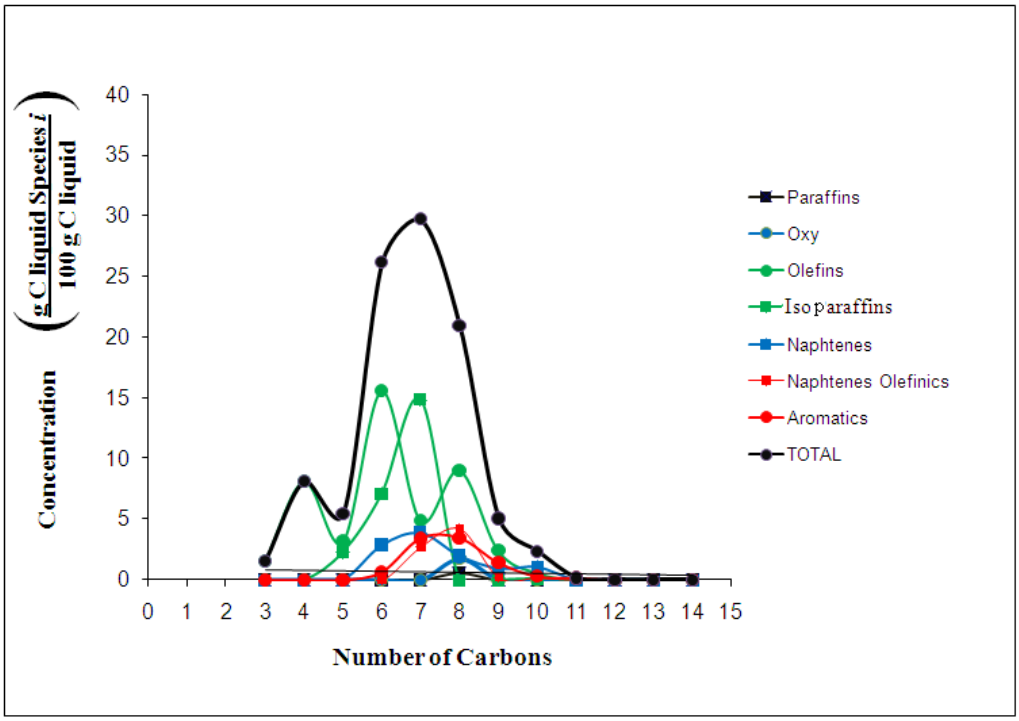

Figure D.13. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 7.5 h^{-1}, P = 1 atm (absolute), T = 370 °C.

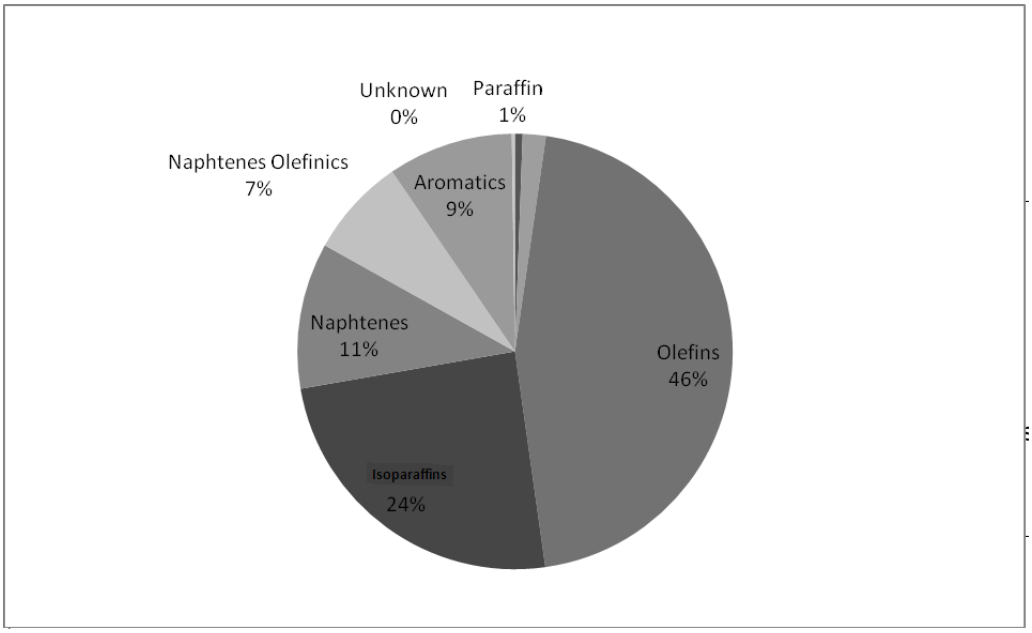

Figure D.14. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 7.5 h^{-1}, P = 1 atm (absolute), T = 370°C.

Table D.9 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 7.5 h^{-1}, P = 1 atm (absolute), T = 370°C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)		Isoparaffins (g C/100 g C liquid)	
3-methyl 2 pentene	9.5	1 methyl cyclopentane	2.8	benzene, 1,3-dimethyl	2.8	2-methyl 2-hexene	7.1
1-butene	8.0	cyclopentane 1 methyl 2 methylene	2.6	benzene, 1-ethyl-2-methyl	2.1	2-methyl pentane	4.4
3 methyl 2 pentene	3.6	cyclopentane 1,2 dimethyl 3 methylene	1.4			2-methyl hexane	2.8
2-pentene	3.1					2-methyl 3- pentene	2.6
1,4 pentadiene 2,3 trimethyl	3.0					2-methyl butane	2.2
2-heptene	2.3					3-methyl hexene	1.9
2-3 dimethyl butene	2.3					2-methyl 2-hexene	1.4
n-propene	1.5					3-methyl hexane	1.0
3-hexene 2,5 dymethyl	1.4						
2,5-dimethyl 3 hexenbe	1.3						
2-heptene 5 methyl	1.0						
3-heptene	1.0						
1-methyl cyclohexene	1.7						
cyclohexene 1,3 dimethyl	1.2						
cyclohexene 1-methyl 4-methylene	1.1						

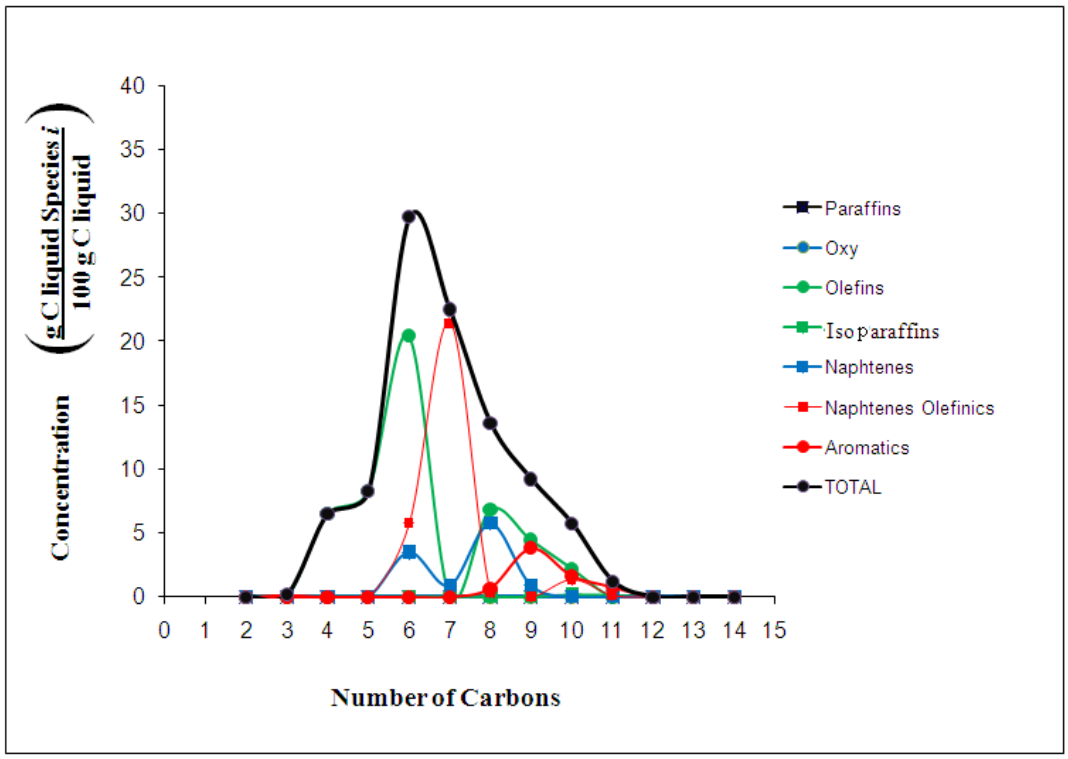

Figure D.15. Liquid product distribution of isopropanol reaction over HZSM-5 (280), WHSV = 11.2 h^{-1}, P = 1 atm (absolute), T = 370°C.

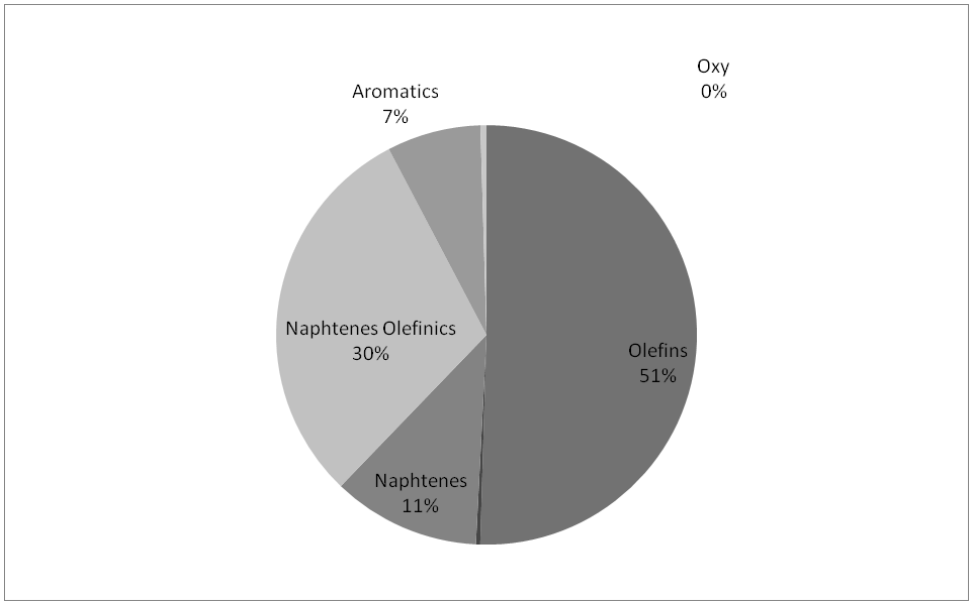

Figure D.16. Liquid product distribution of isopropanol reaction over HZSM-5, WHSV = 11.2 h^{-1}, P = 1 atm (absolute), T = 370 °C.

Table D.10 Most abundant compounds for the isopropanol reaction over HZSM-5 (280), WHSV = 11.2 h^{-1}, P = 1 atm (absolute), T = 370°C.

Olefins and Naphtenes Olefinics (g C/100 g C liquid)		Naphtenes (g C/100 g C liquid)		Aromatics (g C/100 g C liquid)	
2-pentene,3-methyl	8.4	cyclohexane	3.4	benzene, 1-ethyl-2-methyl	2.5
1-butene, 2-methyl	8.2	3,3-dimethyl-1-methelenecyclopentane	3.4		
2-butene	6.5	cyclopentane,1,2-dimethyl-3-methylene	2.2		
1-butene, 2,3-dimethyl	5.4	cyclopropane	1.9		
2-pentene, 3-methyl	3.4				
2-pentene, 2-methyl	3.0				
4-octene	2.4				
3-nonyne	1.4				
3-hexane, 2,5-dimethyl	1.2				
2-hexene, 2-methyl	7.8				
cyclopentene, 1-methyl	5.7				
2-hexene, 3-methyl	3.2				
cyclohexene, 1-methyl	2.2				
cyclohexene, 1-methyl	2.2				
2-pentene, 4,4-dimethyl	1.8				
2-heptene	1.6				
2-hexene, 2-methyl	1.2				

APPENDIX E

TYPE OF HYDROCARBON LIQUID PRODUCTS FROM THE ACETONE REACTION OVER HZSM-5

Table E.1 shows the dominant types of liquid-phase hydrocarbons for each experimental condition.

Table E.1 Most abundant type of liquid-phase hydrocarbons for the acetone reaction

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	A/O						
		350		A/O	A/O	A/O	A/O			
		415		A	A	A	A/O	A/O	A/O	
			0.3	A	A	A				
			1	A	A	A				
	280		0	A	A/O	A/O	A/O	A/O		
			03	A						
			0.5	A	A/O					
			1	A	A/O					
7.8	280		0	A/O		A/O	A/O		A/O	A/O

A= Aromatics
A/O= Aromatics and Oxygenated

Table E.2 shows the most abundant liquid-phase carbon type compounds for all the experiments of acetone reaction over HZSM-5.

Table E. 2 Most abundant type of liquid-phase hydrocarbons for the acetone reaction

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	C9						
		350		C9	C9	C9	C9			
		415		C8	C8	C8	C8	C9	C9	
			0.3	C8	C8	C8				
			1	C8	C8	C8				
	280		0	C8	C8	C9	C9			
			03	C8						
			0.5	C8	C8					
			1	C8	C8					
7.8	280		0	C9		C9	C9		C9	C9

Table E.3 Acetone conversion over HZSM-5 at different conditions.

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	93						
		350		94	83	79	78			
		415		100	100	100	95	88	83	
			0.3	100	100	100				
			1	100	100	100				
	280		0	100	100	88	87			
			03	100						
			0.5	100	100					
			1	100	100					
7.8	280		0	100		93	92		76	62

Table E. 3 Water yield (g H_2O / g hydrocarbon liquid)

P	Catalyst	*T*	H_2 Ratio	WHSV (h^{-1})						
(atm)	Si/Al ratio (mol silica/mol alumina)	(°C)	(mol H_2 / mol acetone)	1.3	2.6	3.9	5.2	6.5	7.9	11.8
1	80	305	0	0.51						
		350		0.44	0.48	0.41	0.44			
		415		0.52	0.47	0.46	0.46	0.48	0.42	
			0.3	0.48	0.45	0.47				
			0.5	0.48	0.47	0.46				
	280		0	0.46	0.47	0.45	0.46	0.44		
			03	0.45						
			0.5	0.43	0.45					
			1	0.45	0.43		0.4		0.4	0.47
7.8	280		0	0.40		0.38	0.5		0.44	0.42

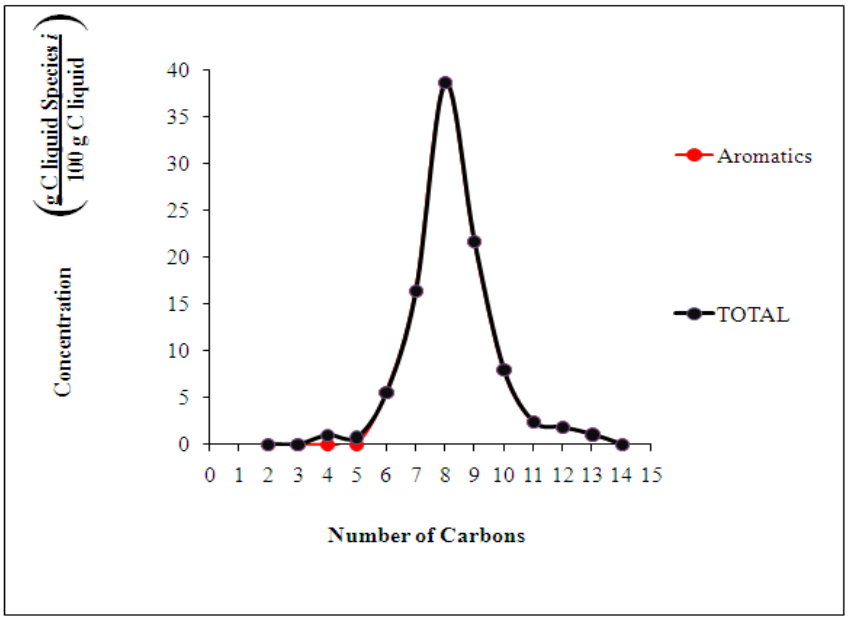

Figure E.1. Liquid product distribution of acetone reaction over HZSM-5(80).

Table E.4 Most abundant compounds for the isopropanol reaction over HZSM-5 (80).

Aromatics (g C/100 g C liquid)	
benzene, 1,4–dimethyl	30.3
benzene, methyl	16.3
benzene, 1,2,4–trimethyl	9.5
benzene, 1,3,5–trimethyl	8.6
benzene, 1,3–dimethyl	8.3
benzene	5.3
naphthalene, 2–methyl	1.5

Figure E.1 shows the typical carbon distribution for C8-centered liquid products. Table E.1 shows the most abundant components C8-centered, which represent 80% of the total liquid hydrocarbons. Figure E.2 shows carbon distribution for C9-centered liquid product. Table E.5 shows the most abundant components for a C_9-type liquid product. These compounds represent 80% of the total amount of liquid hydrocarbons.

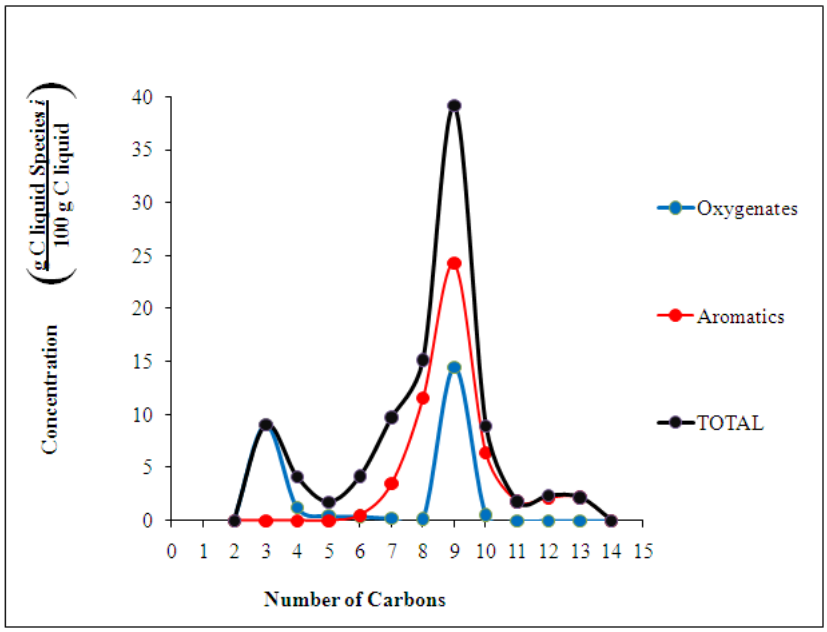

Figure E.2. Liquid product distribution of acetone reaction over HZSM-5(80).

Table E.5 Most abundant compounds for the acetone reaction over HZSM-5 (80).

Aromatics (g C/100 g C liquid)		Oxygenated (g C/100 g C liquid)		Others (g C/100 g C liquid)	
benzene, 1,3-dimethyl	10.5	2-cyclohexen-1-one, 3,5,5-trimethyl	10.5	cyclopropane, (1-methylethenyl)	2.4
benzene, 1,3,5-trimethyl	8.3	2-propanone	9.0	cyclobutane,isopropylidene	2.2
benzene, 1-ethyl-2-methyl	8.2	cyclohexanone, 3,3,5-trimethyl	3.6	cyclopropane, 1,2-dimethyl	1.3
benzene, 1,2,3-trimethyl	6.7	2-butanone	1.2	cyclopentene, 1,5-dimethyl	2.1
benzene, methyl	3.4			1-propene, 2-methyl	2.8
benzene, 1-methyl-3-propyl	1.6				
benzene, 1,2-diethyl	1.5				
benzene, 1,2,3,5-tetramethyl	2.1				
benzene, ethyl	0.9				
naphthalene, 1,2,3,4-tetrahydro-2-m	0.8				

APPENDIX F

ACETONE AND ISOPROPANOL REACTION PROCEDURE

1. Catalyst is weighed and loaded into the reactor. The catalyst is supported by two layers of α-alumina (Figure 3.2).
2. The catalyst is regenerated at 500 °C by flowing air for 2 h at 100 cm^3/min.
3. The system is purged for 2 min with N_2 at 500 cm^3/min
4. The reactor temperature is set. The temperature is controlled by three controllers (top, medium, and bottom). The objective is to maintain the same temperature along the catalyst bed. To get the same temperature, the controllers must be set at the following temperatures:

   Top → T_R – 40°C

   Middle → T_R – 40°C

   Bottom → T_R

   The system has a Type-K thermocouple that measures the temperature along the catalyst bed, which allows verification of a constant temperature along the reactor. The reactor temperature stabilizes after 15 minutes.
5. The liquid reactants are fed to the system with a syringe pump
6. If hydrogen is added to the acetone reaction, the hydrogen is measured with a mass flow controller.
7. After the reaction temperature is stabilized (after 10 minutes of feeding), the liquid products are collected.
8. Then, an on-line analysis of the product stream is performed using a GC connected to the reactor exit. This GC has two detectors: FID and TCD. The analysis intervals are 30 minutes, so the samples can be taken every 30 minutes.
9. The liquid sample is collected and analyzed with a GC-MS. This GC-MS analysis has more detailed compound analysis of the liquid phase.

10. Reactions are terminated by cutting off the feed. Then, the reactor is heated to 500 ℃
11. Finally, air is fed into the system to regenerate the catalyst (return to Step 1).

VITA

Sebastian Taco Vasquez received a B.S. in chemical engineering from Escuela Politecnica Nacional, Quito Ecuador in February 2007. In August 2007, he started his M.S. in the Department of Chemical Engineering at Texas A&M University, receiving his degree in December 2009.

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