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Characterization of Catalysts for Hydrodeoxygenation of Bio-oils using Phenol as a Model Compound

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CHARACTERIZATION OF CATALYSTS FOR HYDRODEOXYGENATION OF

BIO-OILS USING PHENOL AS A MODEL COMPOUND

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Due to the environmental considerations, depletion of fossil fuel reserves and fluctuating non-renewable fuel price, converting non-edible lignocellulosic biomass into renewable energy resources has gained significant importance. Phenol has been chosen as a model compound for catalytic screening because it is abundant in bio-oil composition and shows a high resistance to oxygen removal during hydrodeoxygenation (HDO) reactions. HDO of phenol produces chemicals that can be used as transportation fuels (Aromatics) or fuel additives. Theoretically, HDO of phenol has two distinct reduction pathways: direct deoxygenation (DDO) and hydrogenation (HYD). The previous results published by our group showed a precedent activity and selectivity towards DDO of phenol over Ru/TiO_2 catalyst. They also revealed that the particle size of the Ru/TiO_2 catalyst played an important role for determining the reaction pathways. For instance, nanoparticles of Ru ($\sim$2 nm) supported on TiO_2 leads to DDO pathway, in contrast, large particles ($\sim$30 nm) leads to HYD pathway. In the current thesis, a systematic study was performed to determine the effects of a TiO_2 support and noble metal (Ru) on the

HDO of phenol and to determine the activity and selectivity of the catalyst towards the DDO pathway (Aromatics). Reactions were performed in batch and flow reactors at 300 °C. Evaluation of the catalysts using batch mode showed that the nanoparticles of ruthenium (~2 nm) supported on titanium dioxide (TiO_2) yield significant activity and selectivity for phenol HDO. The main product of this reaction was benzene. Furthermore, the activity and selectivity observed during the deoxygenation of phenol over the ruthenium catalyst were not stable. Therefore, a high-pressure burette along with a 25 mL Parr reactor were used to test the activity and stability of the Ru/TiO_2 catalyst by calculating the hydrogen consumption rate as a function of pressure. During the reaction, the hydrogen consumption rate was decreased which gave an indication that the catalyst was deactivated with time. Subsequently, we have decided to use a packed flow reactor to study the activity, selectivity, and stability of the Ru/TiO_2 catalyst during HDO of phenol. The packed bed reactor results showed that the HYD pathway is the dominant pathway which is not consistent with batch reactor results. It also showed that the catalyst was deactivated during time on stream (TOS). A newly synthesized catalyst of Ru/TiO_2 (UMaine Catalyst) was used to test its activity and stability for phenol HDO. The data for the newly synthesized catalyst were consistent with previous data from our catalyst group. Both catalysts show that the activity of the Ru/TiO_2 catalyst is not stable. Tetrahydrofuran (THF) solvent was then used in the flow reactor and showed better activity and selectivity towards DDO pathway compared with previous results of flow reactor.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

The environmental issues, depletion of fossil fuel reserves and increasing non renewable fuel price serve as motivation for finding a new technology for producing bio-fuels from non-edible biomass [1]. Practically, there are three ways for bio-oil production, fast pyrolysis, gasification and liquefaction of biomass [2]. Among them, advanced pyrolysis processes such as formate-assisted pyrolysis considers one of the most promising process for bio-oil production, which result bio-oils in a very low oxygen content but rich in substituted phenols [3], [4] and [5]. However, the oil produced from these three methods can not be used directly as transportation fuel because it has large amount of highly oxygenated species, which cause many of the undesired properties of bio-oil, such as high viscosity, high corrosiveness, instability and higher heating value (HHV) [6] and [7].

Based on that, hydrodeoxygenation of bio-oil was studied and used as a method for bio-oil upgrading by breaking the C–O bond of oxygenated molecules, however, the variety of bio-oil composition complicates the upgrading. Because phenol and its derivatives are most abundant species in bio-oil composition, and they showed a highly resistance to conversion during HDO reactions. Phenol was then chosen as a model compound for catalytic screening and for providing important information for bio-oil upgrading reactions [8,9]. Generally, Hydrodeoxygenation reaction requires high temperature, high pressure of hydrogen as well as an active and selective of heterogeneous catalysts for upgrading reactions [10].

Several studies have been made for catalytic hydrodeoxygenation, started with conventional catalysts of hydrodesulphurization (sulfides CoMo or NiMo supported on alumina

(Al$_2$O$_3$). These catalysts showed deactivation due to coke deposition and loss of sulfur [11] and [12]. Then, supported noble metal catalysts (Pt, Pd, Ru, and Rh) have been tested for phenol HDO. They consider promising alternatives catalyst because they showed better activity and stability than HDS catalysts, however, metal catalysts are much expensive compared with hydrodesulphurization catalysts [13], [14] and [15].

For phenol hydrodeoxygenation, the researchers seek to develop catalysts with highly activity, stability, and selectivity toward direct deoxygenation of phenol to benzene which reduce the consumption of costly hydrogen as well as provide insight for bio-oil catalytic.

1.2 Hypotheses

1.2.1 Amphoteric Nature of TiO$_2$

The amphoteric nature of TiO$_2$ is considered one of the reasons that making a Ru/TiO$_2$ catalyst is so effective for phenol hydrodeoxygenation. Basically, titanium dioxide has the ability to facilitate H$_2$ heterolysis to generate an active site water molecule that promotes the catalytic C-O bond scission of phenol. The experiments showed that the combination of Ru with the reducible oxide support of TiO$_2$ results in a significant enhancement in both the activity and catalyst stability for the conversion of phenol to benzene [5].

1.2.2 Effect of Ruthenium Particle Size

The second hypothesis deals with particle size of catalysts. Based on the characterization results on the Ru particle size, the experiments showed that small particles of Ru on the support (~2 nm) are very important, where small particles delivered higher activity and selectivity for phenol HDO and the main product was benzene. This unprecedented activity may be attributed to the increased interface areas between the Ru particles and the TiO_2 support. [5].

1.3 Research Motivations

- Produce transportation fuels (aromatics) out of pyrolyzed bio-mass.
- Study and evaluate the effectiveness of catalysts for phenol hydrodeoxygenation to end up with a reactive and stable catalyst used for bio-oil upgrading.

1.4 Research Objectives

- Evaluate and measure reaction kinetics of Ru/TiO_2 catalyst for converting phenol to benzene.
- Determine the activity and selectivity of phenol HDO products using Ru/TiO_2 catalyst.
- Collect continuous reaction data, and compare with batch reaction data using the same catalyst.

CHAPTER 2

REACTOR HYDRODEOXYGENATION OF PHENOL WITH Ru/TiO$_2$ BATCH

2.1 Introduction

This chapter covers characterization of catalysts for hydrodeoxygenation of bio-oils using phenol as a model compound. First, literature related to characterization of catalysts is reviewed. Second, experimental methods and apparatus used for screening catalysts are discussed. Products analysis of phenol hydrodeoxygenation are discussed. Finally, the experiment's results are discussed.

The initial objective of this project is to determine the mechanism of the Ru/TiO$_2$ catalyst that has such a high activity towards DDO of phenol to benzene. The initial results of phenol HDO indicate that it is difficult to reproduce the results in the batch reactor. Therefore, new experiments of phenol hydrodeoxygenation were done in the batch reactor along with a high-pressure burette and showed that the reaction rate changed with time which means that the catalyst was not stable. Then, a packed bed reactor was used to study the activity, selectivity, and stability of the Ru/TiO$_2$ catalyst for phenol HDO. In fact, the packed bed reactor showed very different selectivity than in the batch reactor and also showed that the catalyst lost its activity with time.

2.2 Literature Review

Many researchers have devoted significant effort for investigating reactive and stable catalysts for bio-oil upgrading. As a result of that, a lot of catalysts were synthesized and tested for bio-oil upgrading. Firstly, conventional hydrodesulfurization (HDS) catalysts (sulfides of CoMo or NiMo supported on Al_2O_3) have been used for bio-oil upgrading. These catalysts showed high activity in HDO reactions, however, they cannot be used for bio-oil upgrading, the low content of sulfur in bio-oil makes the sulfide structure of the catalyst unstable which requires addition of sulfur to keep the catalyst active, which ultimately leads to sulfur contamination and quickly deactivation. Moreover, the experiments showed that supported Al_2O_3 is unstable against the abundant amount of water in bio-oil under HDO reaction conditions [16] and [17].

As stated above, phenol and its derivatives have attracted significantly attention than bio-oil composition due to their recalcitrant for removal of oxygen at the desired bio-oil reaction conditions as well as to understand the catalytic screening of HDO reaction. Applying hydrodesulfurization (HDS) catalysts for catalytic phenol showed that activity and stability of CoMo/ Al_2O_3 catalysts are better than NiMo/Al_2O_3 [18]. However, these catalysts are quickly deactivated under HDO conditions. Another attempts of phenol HDO have been also applied with sulfides (CoMo and NiMo) catalysts but at different supports. Zirconia, titania and active carbon supports on (CoMo and NiMo) catalysts show better hydrothermal stability than Al_2O_3 support. Additionally, CoMo/ZrO_2 and CoMo/TiO_2 catalysts showed higher catalytic activity in HDO reactions than CoMo/Al_2O_3 [19]. Moreover, Co and Mo catalysts on activated carbon [20] showed improved selectivity of phenol HDO products but it gave lower activity than Al_2O_3 support catalyst. Nobel metal catalysts such as (Rh, Pt, Pd, and Ru) has been also studied for phenol HDO using different reducible (TiO_2 - ZrO_2) and non-reducible (carbon-silica) supports.

These catalysts were known to be active at low temperatures which lead to prevent coke formation and deactivation. However, noble metal catalysts are expensive compared with others [21], [22] and [23].

The experiments revealed that the combination of reducible support [TiO_2] with nano metal catalyst [Ru] which defined herein as a bifunctional catalyst are very important to get DDO pathway. Thus, ruthenium supported on TiO_2 showed a significant performance for both activity and selectivity of DDO of phenol, this agrees with recent experimental and DFT studies on Ru/TiO_2 rutile (110) surfaces [5]. The unprecedented activity and selectivity of Ru/TiO_2 attribute to the amphoteric nature of TiO_2. R. Nelson and his group suppose that TiO_2 can facilitate heterolysis dissociation of H_2 to generate an active site water molecule on the support which reinforce the catalytic C–O bond scission of phenol.

Theoretically, hydrodeoxygenation of phenol has two major reaction routes: (1) direct hydrodeoxygenation (DDO) and (2) hydrogenation followed by dehydration (HYD). Scheme (1) shows the two major reaction pathways by which oxygen can be eliminated from phenol. The upper route shows the direct hydrogenolysis of the C-O bond of phenol to form aromatic product benzene and water. This pathway consumes a single hydrogen equivalent for reduction. The lower route proceeds by a catalytic hydrogenation of the aromatic ring to produce cyclohexanone. Further reduction and dehydration of cyclohexanone provide the second product, cyclohexene, additional reduction of cyclohexene leads to the last deoxygenated product, cyclohexane. Overall, the lower route consumes four hydrogen equivalents for deoxygenation [5].

6
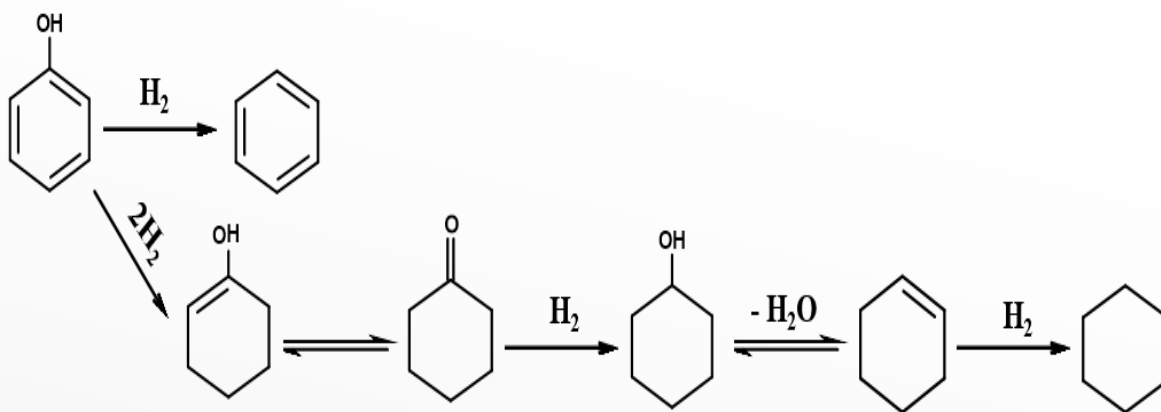
Figure 2.1 Proposed pathways for phenol HDO reaction. The top pathway shows the direct deoxygenation route (DDO) and the lower pathway gives the hydrogenation route (HYD). From reference 5.

2.3 Experimental

2.3.1 Materials

Catalytic deoxygenation of phenol was performed in a batch reactor at ruthenium supported by TiO_2. The catalyst was synthesized by R.N. Austin's group in the Department of Chemistry at Bates College, ME. Titanium dioxide (21 nm particle size, 33-55 m^2 g^{-1} surface area), $RuCl_3 \cdot 3H_2O$, and trace metal grade hydrochloric acid were all purchased from Sigma-Aldrich. The catalyst synthesized by incipient wetness impregnation method. The catalyst had 1.34% metal loading, 47 m^2/g surface area, 1.5 nm average particle diameter and 453 K reduction temperature.

2.3.2 Methods

2.3.2.1 Activation of Ru/TiO₂ Catalyst

Two techniques were used to activate and prepare the Ru/TiO_2 catalyst for reaction. The first technique is called in-situ reduction. In-situ reduction was done inside the batch and flow reactors. For the 25 mL Parr reactor (batch reactor), the catalyst was reduced under 550 psig H_2 at 300 °C for 1 hour. Whereas in the flow reactor (packed bed), the catalyst was reduced in flowing H_2 at 450 psig and 300°C for 5 hours. Both types of reductions showed similar performance for phenol HDO for both the Bates and UMaine catalysts. Some catalysts were also reduced ex-situ by flowing hydrogen through a cell maintained at 400°C. The ex-situ reduced catalysts were passivated by gradually exposing them to air. The procedural details are in Appendix C.

2.3.2.2 Apparatus for Screening of Catalysts for Phenol Hydrodeoxygenation

Hydrodeoxygenation of phenol was carried out in a 25 mL Parr reactor. The system is illustrated in Figure 2.2. It consists of a 25 mL Parr reactor equipped with a gas entrainment stirrer, inlet and outlet ports for feeding or removing gas from the system and a water cooling loop, which controls the temperature within ± 0.5 °C, pressure gauges, internal thermocouple and two gas cylinders of H_2 and N_2. The Parr reactor assembly is connected to a Parr process controller, which maintains the agitation rate in the reactor, sustains and records the temperature in the reactor, and records the pressure in the reactor.

8
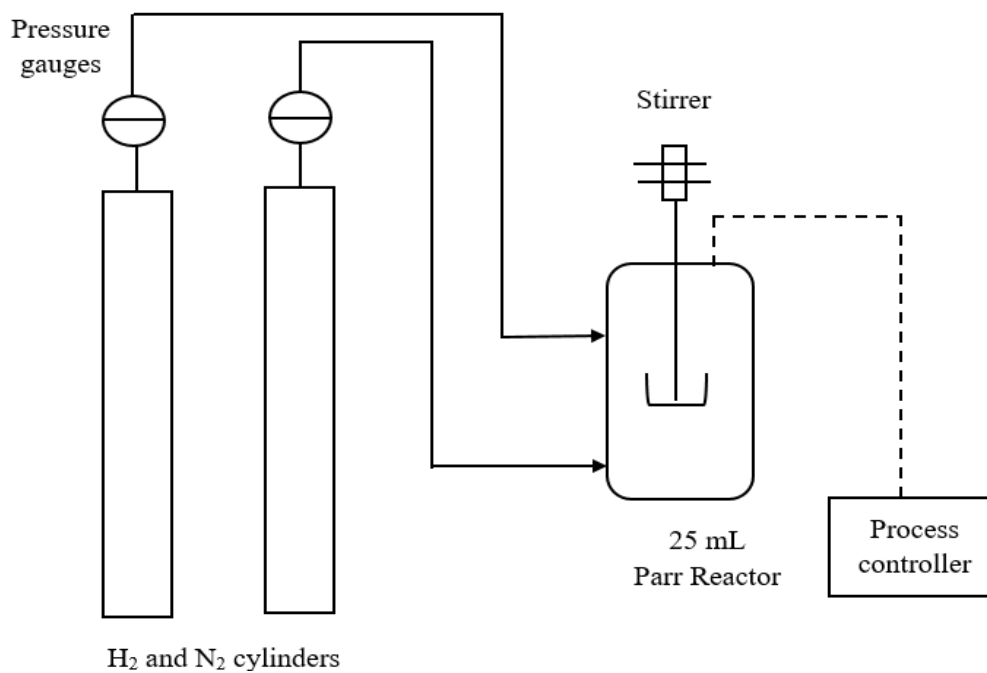
Figure 2.2 System for liquid-phase reaction characterization
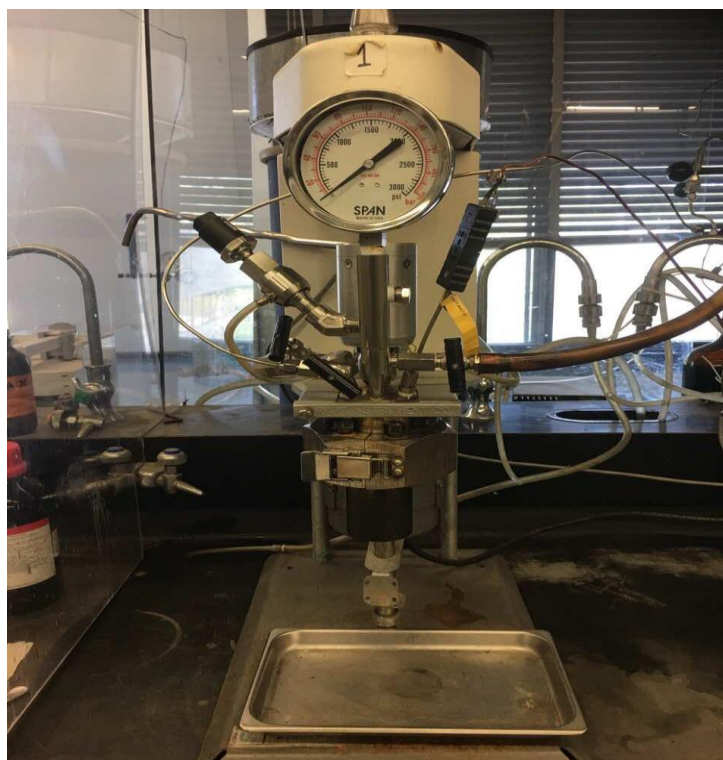
Figure 2.3 25 mL Parr reactor system

In a typical test, 5 mL of liquefied phenol (10 wt. % water) was loaded into an autoclave 25 mL Parr reactor along with 100 mg of freshly reduced catalyst (in situ reduction). The reactor was flushed with N_2 three times to remove oxygen from the vessel, and then pressurized with nitrogen to 15-20 psig at room temperature and heated to the desired reaction temperature, 300 °C. After the temperature stabilized, H_2 was introduced from a cylinder into the reactor through a valve while stirring the reactants at 750 rpm. The total pressure was adjusted to 650 psig by regulating the H_2 pressure. The pressure was kept constant over the course of a 1 hour reaction. After the reaction, the reactor was cooled down to room temperature and the gas in the reactor released very slowly. The liquid products were collected and filtered to obtain the solid catalyst for saving and the liquid products were analyzed by gas chromatography with a flame ionization detector (GC-FID).

2.3.2.3 Determining Hydrogen Consumption Rate of Phenol Hydrodeoxygenation

A 500 mL high pressure gas burette was used along with a 25 mL Parr reactor to calculate the hydrogen consumption rate of phenol hydrodeoxygenation. This method has been used to test both activity and stability of catalysts for phenol hydrodeoxygenation. The high-pressure burette provides constant pressure to the reactor during reaction and also provides a way to measure the hydrogen consumption rate by observing the pressure drop in the burette during the reaction. Another a graduate student at UMaine, Mohit Bhatia. (2011) "Thermal Conversion of Carboxylate Salts and Catalytic Ketone Hydrogenation". Retrieved from University of Maine Electronic Theses and Dissertations.1567, calibrated the high-pressure burette to correlate the rate of pressure drop in the burette to the rate of hydrogen consumption and came up with

equations (2.1) and (2.2). Equation (2.1) was used to normalize the measured pressure of burette

to a temperature of 20°C.

$$P_{20°C} = P \frac{293.15}{T} \tag{2.1}$$

Where P [kPa] is the measured pressure, $P_{20°C}$ [kPa] is the correct pressure, and T[K] is the

burette measured temperature.

Equation (2.2) was used to accurately calculate the moles of hydrogen consumed during the

reaction.

$$n_{H2} = -2.210 * 10^{-4} (P_1 - P_0)_{20°C} + 1.608 * 10^{-9} (P_1^2 - P_0^2)_{20°C} \tag{2.2}$$

Where n_{H2} [mol], moles of hydrogen consumed during the reaction between two measured

pressure P_0[kPa] and P_1[kPa].

Equations 2.1 and 2.2 were used to calculate the hydrogen consumption rate for the batch

reactions.
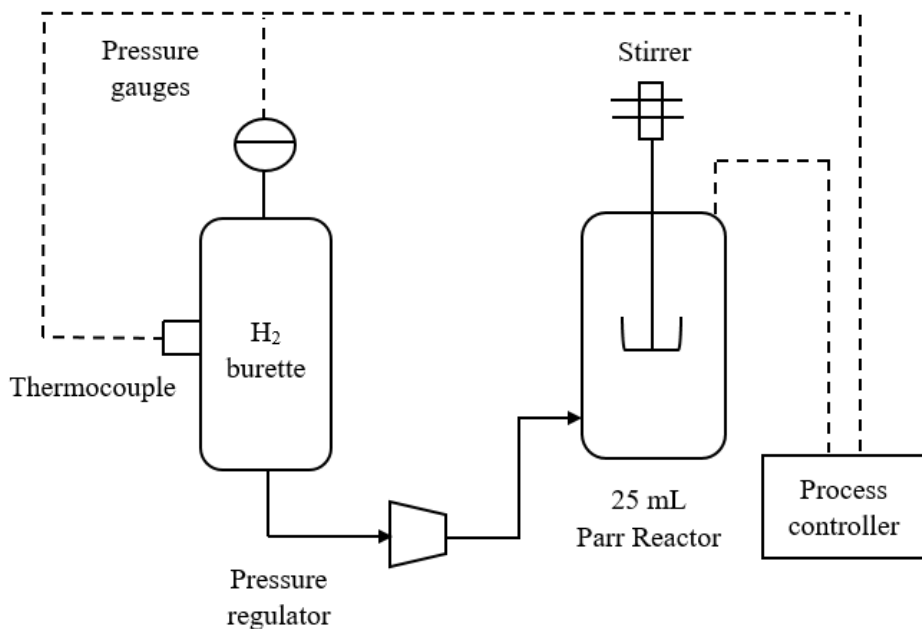
Figure 2.4 Apparatus for determining hydrogen consumption rate for phenol HDO reaction
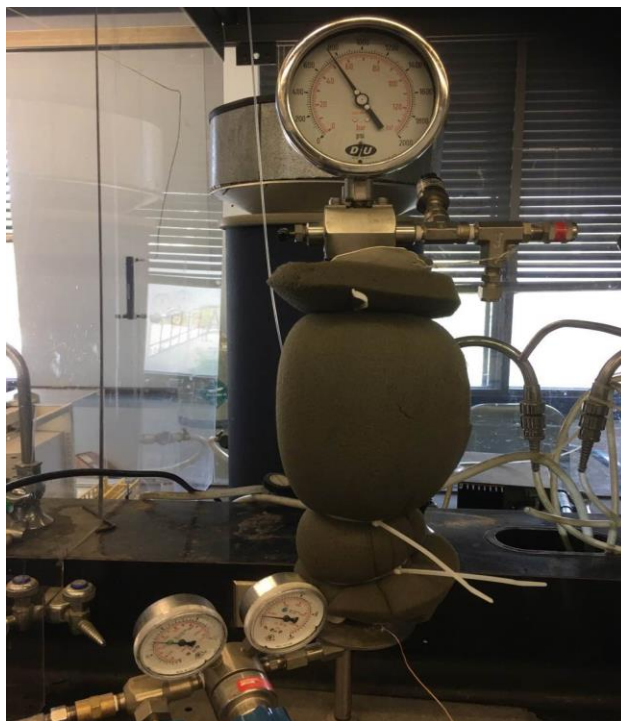
Figure 2.5 High pressure gas burette-Parr instrument

2.4 Product Analysis

The liquid products from HDO of phenol were analyzed by a Shimadzu GC-2010 apparatus equipped with a flame ionization detector FID (Agilent J&W GC Column, 30m X 0.25 mm). The samples were injected with an initial temperature set to 40 °C and were held for 1 minute. The temperature was increased to 120 °C at a rate of 5 °C/min and held for 2 minutes. The temperature was increased again from 120 °C to 180 °C at a rate of 5 °C/min and held for 2 minutes Finally, the temperature goes from 150 °C to 250 °C at a rate of 25 °C/min and held for 2 minutes. The samples were diluted with ethyl acetate in 1:100 volume ratio and injected for detection. Helium was chosen as the carrier gas. Pure components of reactant and products were used for peak calibration.
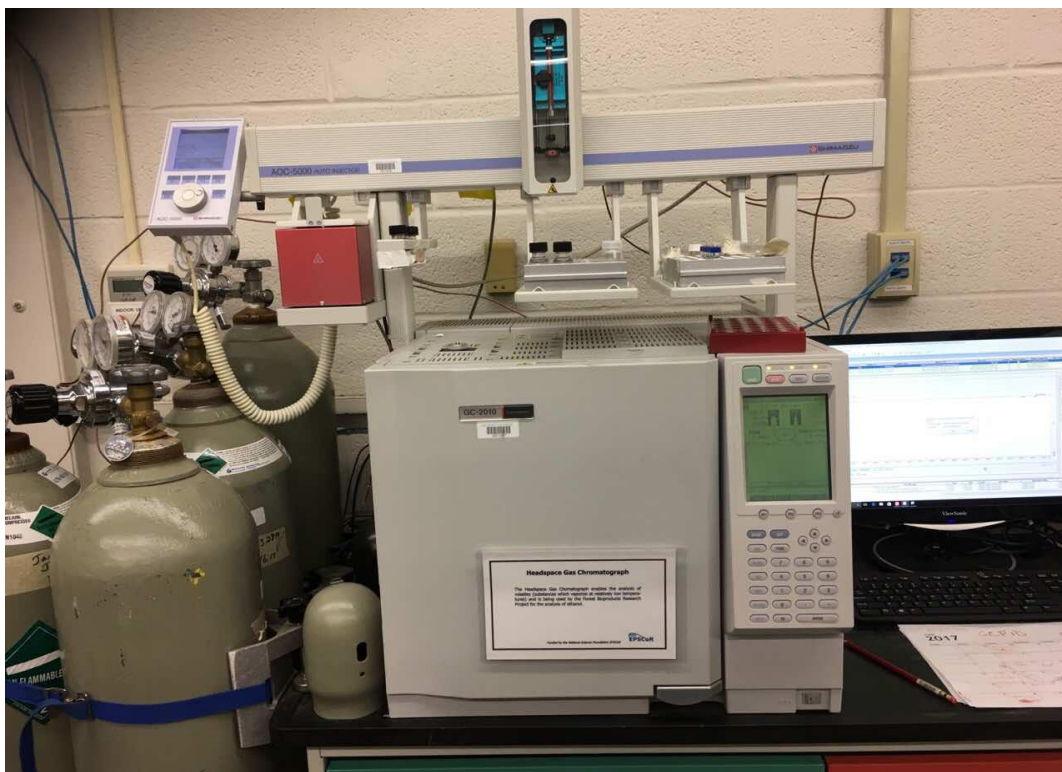
Figure 2.6 Shimadzu GC-FID used for phenol HDO products analysis

2.5 Results and Discussion

Two procedures outlined in 2.3.2.2 and 2.3.2.3 were used for catalytic screening of Ru/TiO₂ for the phenol HDO reaction. There were two techniques used for reducing and activating the Ru/TiO₂ catalyst. The first is in-situ reduction and the other is ex-situ reduction. Both methods of reduction showed a similar activity and selectivity for phenol HDO.

Table 2.1 shows the average percent of phenol HDO products, conversion, deoxygenation and the ratio of benzene to all other products from the HDO of phenol over the Ru/TiO₂ catalyst. The average percent of phenol HDO products were calculated as the ratio of the specific products to that of the total products. The phenol conversion was calculated as {[initial phenol -

13

final phenol]/initial phenol} *100. The deoxygenated products were defined as all oxygen free products including benzene, cyclohexane, and cyclohexene. The ratio of DDO: HYD is the ratio of benzene to the sum of hydrogenation products (cyclohexane, cyclohexene, cyclohexanol, and cyclohexanone).

Table 2.1 Product distribution of phenol HDO reaction over Ru/TiO$_2$ catalyst at 1 hour reaction time

Catalyst	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol	% Cyclohexanone	% Conversion	% Deoxygenation	DDO / HYD
RuCl$_3$/TiO$_2$ Bates catalyst	63	0.0	4.9	15.4	16.7	13.8	67.9	1.7
RuCl$_3$/TiO$_2$ Bates catalyst	73	5.7	3.6	7.5	10.2	18.5	82.3	2.7
RuCl$_3$/TiO$_2$ Bates catalyst	90.4	7.8	0	0.6	1.2	15.4	98.2	9.4
RuNo(No$_3$)$_3$/TiO$_2$ UMaine catalyst	50.8	30.6	1.7	11.5	5.4	10.2	83.1	1.0
RuNo(No$_3$)$_3$/TiO$_2$ UMaine catalyst	71.2	20.7	1.6	3.3	3.2	11.9	93.5	2.5
RuNo(No$_3$)$_3$/TiO$_2$ UMaine catalyst	81.3	12.8	1.8	1.6	2.5	15.3	95.9	4.4

The experiment conducted in the batch reactor showed that benzene was the major product of phenol HDO and, requiring the Ru/TiO$_2$ catalyst that was synthesized (in Bates) by our group or the newly synthesized catalyst (synthesized in UMaine). It also revealed that the ratio of phenol HDO products changed in each experiment under the same catalyst and reaction conditions. For instance, the highest ratio of benzene reached 90.4, while the lowest ratio was 50.8. It was also observed that the average percent of deoxygenated products and the ratio of

DDO: HYD were different. These observations clearly indicate that the activity of the Ru/TiO$_2$ catalyst was not stable.

The mole fraction of phenol HDO products was then calculated to test the catalytic performance of Ru/TiO$_2$ under the same reaction conditions. It was calculated by dividing a specific product by phenol fed. Figure 2.7 shows the liquid product distribution of phenol HDO in terms of mole fraction reached over Ru/TiO$_2$ catalyst synthesized in Bates and UMaine. The results indicate that the mole fraction was different in each experiment. By taking into account all experiment results, it is quite clear that the activity of the Ru/TiO$_2$ catalyst was not stable.
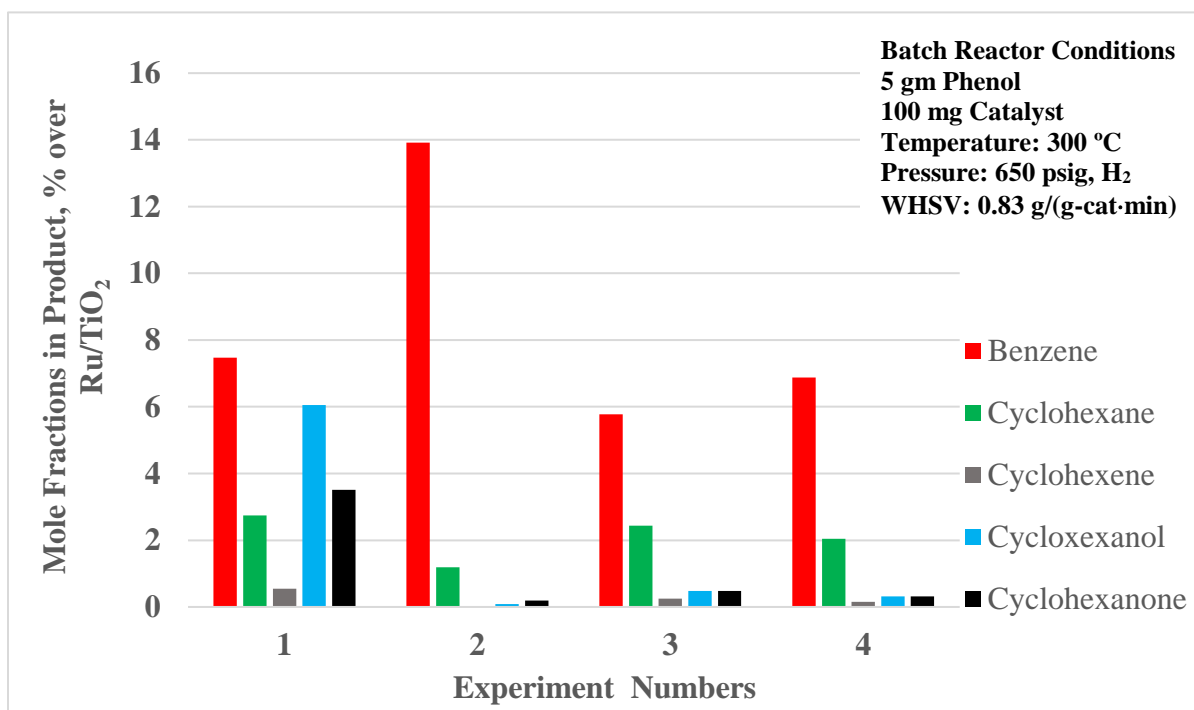
Figure 2.7 Mole fractions of phenol HDO product at 1 hour

Our collaborators at Bates and Barnard Colleges were running reactions on the Ru/TiO$_2$ catalysts in parallel with our experiments. Their batch experiments were run under similar conditions, but only for 15 minutes duration, compared to 60 minutes for our experiments.

Therefore, we ran some experiments for 15 minutes duration. Table 2.2 presents the average percent of phenol HDO products, deoxygenation products and conversion of phenol. The results also showed that Ru/TiO$_2$ catalyst provide a highly activity towards both DDO pathway and benzene selectivity. It also observed that the liquid product distribution, phenol conversion, deoxygenation, and ratio of DDO: HYD were different at same reaction condition. Since the conversion was different in these experiments, we spent a lot of time trying to understand whether the reaction was susceptible to small changes in catalyst pretreatment or reaction ramp rates. Indeed, some experiments would show a significant increase in pressure and temperature as the reactor approached 300°C, and others would not.

Table 2.2 Product distribution of phenol HDO reaction over Ru/TiO$_2$ catalysts at 15 minutes reaction time.

Catalyst	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol	% Cyclohexanone	% Conversion	% Deoxygenation	DDO / HYD	Reaction rate mol/gm*min
RuCl$_3$/TiO$_2$ Bates catalyst	55.7	0.0	0.0	16.1	28.2	4.5	55.7	1.3	0.001561
RuCl$_3$/TiO$_2$ Bates catalyst	52.8	0.0	0.0	18.1	29.1	4.3	52.8	1.1	0.001592
RuCl$_3$/TiO$_2$ Bates catalyst	79.2	5.0	0.0	5.9	9.9	8.6	84.2	3.8	0.003200
RuCl$_3$/TiO$_2$ Bates catalyst	33.4	0.0	0.0	33.8	32.8	6.7	33.4	0.5	0.002396
RuCl$_3$/TiO$_2$ Bates catalyst	34.8	0.0	0.0	32.3	32.9	7.0	34.8	0.5	0.002527
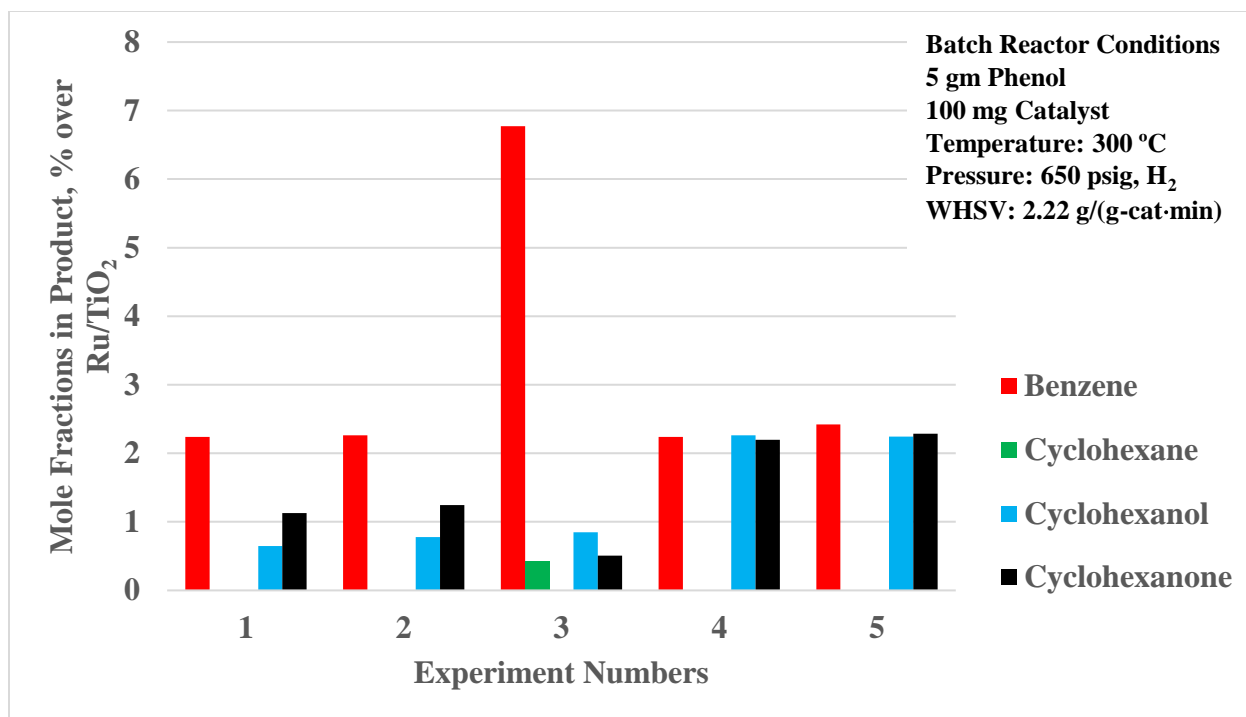
Figure 2.8 Mole fractions of phenol HDO products at 15 minutes for the data in Table 2.2.

The results showed in Figure 2.8 confirm that the liquid product distribution of phenol HDO at 15 minutes was different which is consistent with the experiments that done at 1 hour. It is also important to point out that, cyclohexene was not detected in all experiments that done in 15 minutes. In contrast, cyclohexene was not detected in one experiment that done in 1 hour. Experiment 3 seems to have significantly higher benzene yield compared to the other experiments done at the same condition. This could be attributed to something might have happened during the experiment or the activity of Ru/TiO$_2$ catalyst was not stable.

2.6 Reaction Rate of Phenol Hydrodeoxygenation in Batch Reactor

The initial reaction rate of HDO of phenol over the Ru/TiO_2 catalyst was estimated in a 25 mL Parr reactor at 15 minutes assuming that the rate was constant for low conversion. Therefore, the rate was calculated as:

$$\text{Initial rate} = \frac{\text{Total molar of products formed}}{\text{Weight of catalyst x Time of reaction}}$$ 1

The reaction rate of phenol hydrodeoxygenation was accomplished by using the same batch reactor conditions [300 °C, 650 psig (H_2), 100 mg of Ru/TiO_2, 5 mL of phenol] except the time of reaction which was lowered to 15 minutes.

The products of phenol HDO were benzene, cyclohexane, cyclohexanol, and cyclohexanone, while cyclohexene was not detected. After the reaction, the liquid product was immediately collected at 300 °C to calculate the reaction rate at the reaction temperature.

Table 2.3 shows the reaction rate of duplicating reactions at the same reaction conditions.

Table 2.3 Initial reaction rate of phenol HDO products over Bates catalyst at 15 minutes reaction time.

Catalyst	Reaction rate mol/gm$_{cat.}$*min
Ru/TiO$_2$	0.00159
Ru/TiO$_2$	0.00156

Interestingly, similar results of reaction rate have been obtained for phenol HDO at the same reaction conditions. This observation reveals that the activity of Ru/TiO₂ catalyst was stable. It is possible that collecting liquid product at reactor's temperature could influence on the activity of catalyst to end up with different product distribution.

As stated above, the Ru/TiO₂ catalyst showed different activity and selectivity for phenol HDO reactions. Therefore, the reaction rate calculated using the procedure in section 2.3.2.3 is plotted versus reaction time in Figure 2.9. The calculation showed that the reaction rate of phenol HDO was decreased over the process of a 1 hour experiment. This indicates that the activity and stability of Ru/TiO₂ catalysts were not stable and the catalyst deactivated with time.
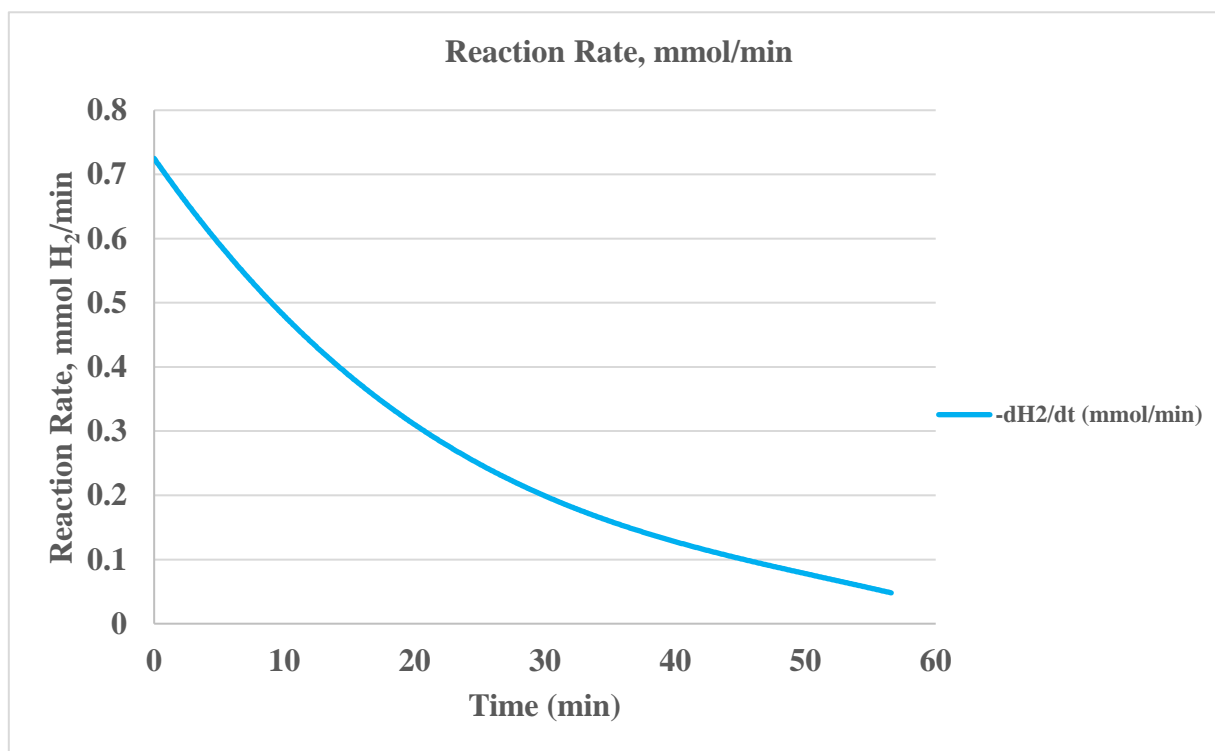
Figure 2.9 Reaction rate of phenol HDO vs. time in a batch reactor containing 5 gm phenol and 100 mg catalyst at 300°C and 650 psig.

19

Figure 2.10 shows the chromatogram obtained via phenol HDO reaction at batch reactor with

Bates catalyst at 1 hour duration.
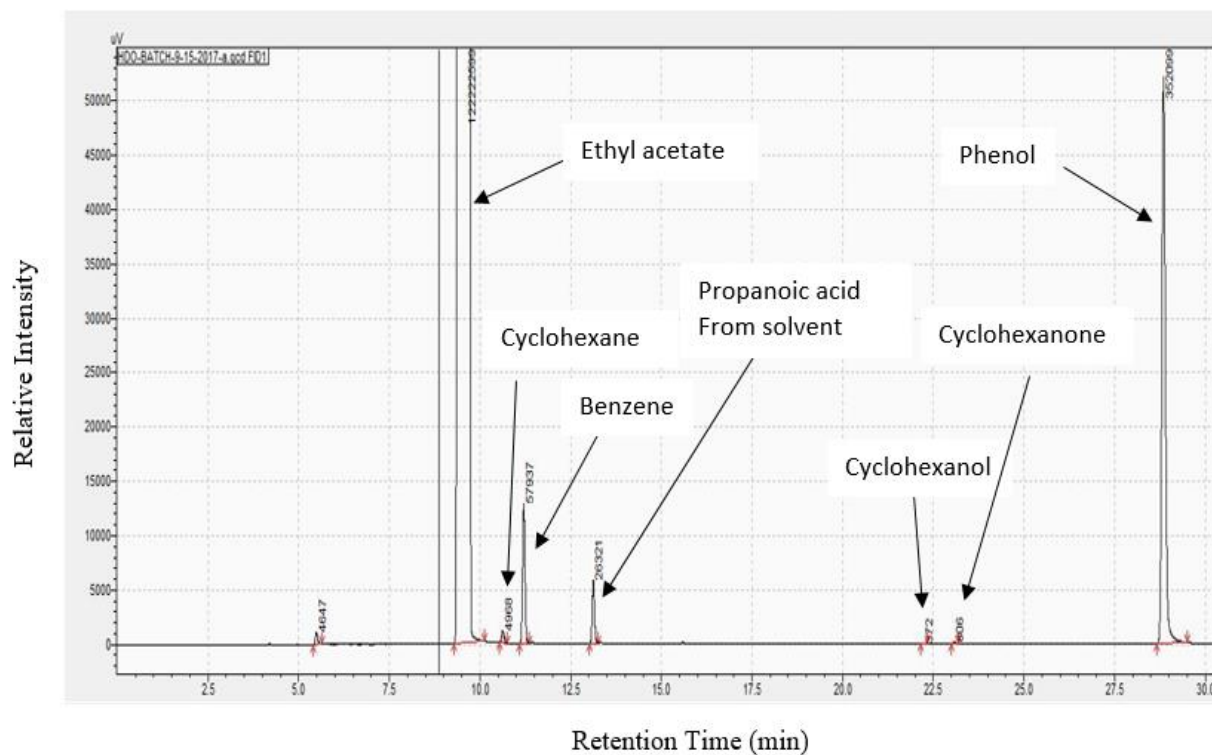
Figure 2.10 GC-FID chromatogram of phenol HDO products over Ru/TiO_2 (Bates catalyst) at 1

hour.

CHAPTER 3

PACKED BED REACTOR HYDRODEOXYGENATION OF PHENOL WITH Ru/TiO$_2$

3.1 Introduction

This chapter deals with characterization of catalysts for hydrodeoxygenation of bio-oils using phenol as a model compound using a packed bed reactor. First, the reason for using a packed bed reactor for phenol hydrodeoxygenation is discussed. Second, the materials and synthesis catalyst are discussed. Third, the experimental methods and apparatus used for screening catalysts are discussed. Finally, the experiment's results are discussed.

3.2 Packed Bed Reactor for Phenol Hydrodeoxygenation

As stated above, the experimental results showed that the activity and stability of catalysts for phenol hydrodeoxygenation were not stable. Moreover, they showed that the liquid product distribution of phenol hydrodeoxygenation, using the same catalyst and reaction conditions, were different in each experiment. It is well known that the batch reactor runs for a short-time. Therefore, it did not give adequate information about catalyst stability. In contrast, the flow reactor is favorable because it allows long-term studies. It also provides better kinetic control of reaction steps, which helps to clearly explain complex reaction networks. Due to those reasons, we have decided to use a flow reactor (packed bed reactor) to study the activity and stability of catalysts for phenol hydrodeoxygenation.

3.3 Materials

Catalytic deoxygenation of phenol as a model compound of bio-oil was performed in a packed bed reactor using ruthenium metal supported by TiO_2. The catalysts were synthesized by R.N. Austin's group in the Department of Chemistry at Bates College, ME, as mentioned above in Chapter 1. Some catalysts were also synthesized by Abdulazeez Khlewee in the Department of Chemical and Biological Engineering at University of Maine. The UMaine catalyst was prepared with a solution of ruthenium nitrosyl nitrate $RuNo(No_3)_3$ and titanium dioxide P25, which was donated by Evonik.

3.3.1 Synthesis of $RuNo(No_3)_3/TiO_2$ Catalyst (UMaine Catalyst)

The catalyst was synthesized by the Incipient Wetness Impregnation Method (IWI). This common technique gives an accurate amount of the metal loading on the support. First, the active metal precursor of titanium supported was added to deionized water for the purpose of determining the total pore volume (TPV). Second, the aqueous solution-containing 1.5% of metal $RuNo(No_3)_3$ was added dropwise to the titanium support containing the same pore volume as the volume of the solution that was added. Third, the catalyst was left overnight to dry in an oven at 100 °C to drive off the volatile components within the solution. Finally, the catalyst was crushed to small particles and used in the reactions.

3.4 Methods

3.4.1 Continuous Flow Reaction Characterization

The hydrodeoxygenation of phenol was carried out in an upflow packed bed reactor. The setup consisted of a stainless-steel tubular reactor (i.d. = 0.2 mm, L = 150 mm, V = 0.005 mL, material: SS316) that was heated by heating tape. The setup also consisted of two gas cylinders of H_2 and Ar along with two mass flow controllers, pressure gauges, a liquid collector, a graduated cylinder to measure the amount of reactant fed into the reactor, and a pump (M1-Class), which is used to facilitate the flow of phenol into the reactor. The reactor temperature was controlled using a digital controller. A thermocouple was used to measure and control the temperature of the catalyst bed by touching it the external surface of reactor.
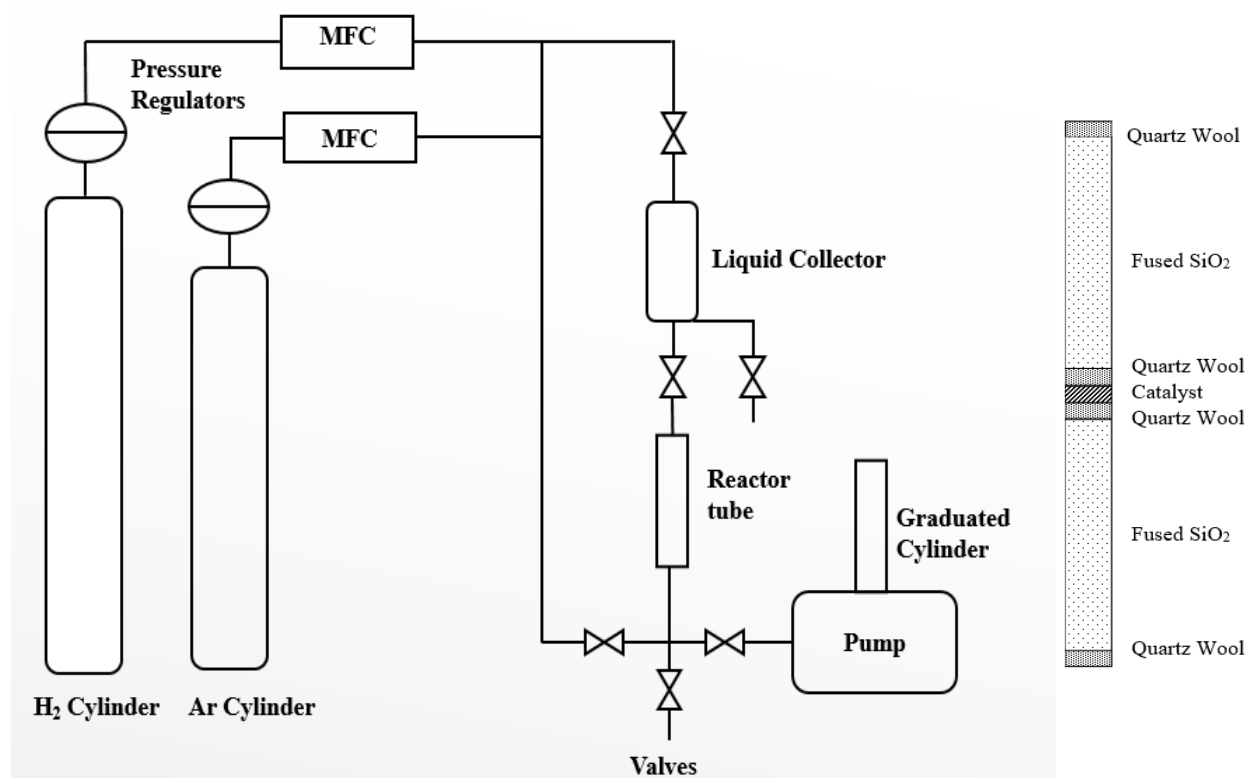
Figure 3.1 Apparatus for liquid phase reaction characterization (packed bed reactor)

3.4.2 Catalyst Activity Measurements

The reactor was packed with 25 mg of Ru/TiO$_2$ catalyst was mixed with 250 mg of crushed fused silica to expand the reaction zone. The catalyst was placed between two pieces of quartz wool, bracketed by two silica layers and quartz wool plugs at each reactor end. The reactor was pressurized to 450 psig with H$_2$, and heated to the reaction temperature 300 °C at 1.5 °C/min. After the temperature stabilized, these conditions were maintained for at least five hours, and up to 24 hours to pretreat the catalysts. Then, phenol was pumped into the reactor at 0.04 mL/min. The liquid effluent was collected every hour from the separator and analyzed by GC-FID.

3.5 Results and Discussion

In this work, hydrodeoxygenation of phenol was investigated using a packed bed reactor to study the activity, selectivity, and stability of Ru/TiO$_2$ catalyst. A weight hourly space velocity (WHSV) of the batch reactions was calculated to determine the equivalent mass flow rate of phenol needed to relate the results from the continuous flow reactor to those of the batch reactions. The first experiment of phenol HDO reaction was conducted as follows: reaction temperature 300 °C, reaction pressure 450 psig H$_2$, mass of catalyst 25 mg, phenol flow rate 0.04 mL/min.

Table 3.1 Product distribution of phenol HDO reaction over Ru/TiO$_2$ (Bates catalyst) at 1 hour sampling.

Time on Stream hr.	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol	% Cyclohexanone	% Conversion	% Deoxygenation	DDO / HYD
1	3.96	2.32	0.32	19.44	8.84	34.89	6.61	0.13
3	5.85	2.14	0.51	36.82	15.00	60.33	8.50	0.11
5	6.69	2.48	0.64	36.73	14.88	61.42	9.81	0.12
7	5.97	1.84	0.62	32.47	14.60	55.50	8.44	0.12
20	4.31	1.08	0.45	25.11	13.12	44.07	5.85	0.11
22	4.48	1.28	0.45	26.17	12.61	44.99	6.21	0.11
24	4.50	1.41	0.46	26.60	12.34	45.30	6.37	0.11
28	4.29	1.30	0.42	25.75	12.20	43.96	6.01	0.11
44	3.45	0.90	0.41	19.76	10.85	35.37	4.77	0.11
49	3.40	1.00	0.35	21.32	10.41	36.47	4.74	0.10
51	3.32	0.98	0.31	20.68	9.95	35.25	4.62	0.10
53	3.14	0.93	0.28	20.80	9.90	35.05	4.35	0.10
54	1.71	0.00	0.00	19.93	9.74	31.39	1.71	0.06
66	2.10	0.61	0.18	16.00	8.84	27.72	2.88	0.08
70	2.59	0.82	0.24	18.08	8.87	30.60	3.65	0.09
74	0.18	0.00	0.00	9.92	4.91	15.00	0.18	0.01
78	2.16	0.63	0.19	11.80	6.34	21.12	2.97	0.11
83	2.39	0.67	0.21	14.42	7.17	24.85	3.26	0.11
96	2.16	0.63	0.00	14.85	7.08	24.72	2.79	0.10
102	2.01	0.62	0.00	15.13	6.96	24.73	2.63	0.09
117	1.97	0.57	0.00	13.28	6.65	22.47	2.54	0.10

Table 3.1 shows the percent of phenol HDO products, conversion, deoxygenation and the ratio of benzene, to all other products from the HDO of phenol over the Ru/TiO$_2$ catalyst reached over a continuous flow reactor. The experiment showed that cyclohexanol and cyclohexanone were the major products in phenol HDO. It also confirms that the average percent of deoxygenated products and the ratio of DDO: HYD were less than that achieved using the batch reactor.

Figure 3.2 illustrates the product distribution for HDO of phenol in terms of selectivity reached over Ru/TiO$_2$ catalyst, synthesized by our catalyst group at Bates. The selectivity of each product is calculated by dividing the molar flow rate of the product per consumption of phenol. A high selectivity towards cyclohexanol and cyclohexanone was observed ~60% and ~30%, respectively, while we got a low selectivity towards benzene ~10%. We can conclude that the HYD of phenol is the dominant pathway.
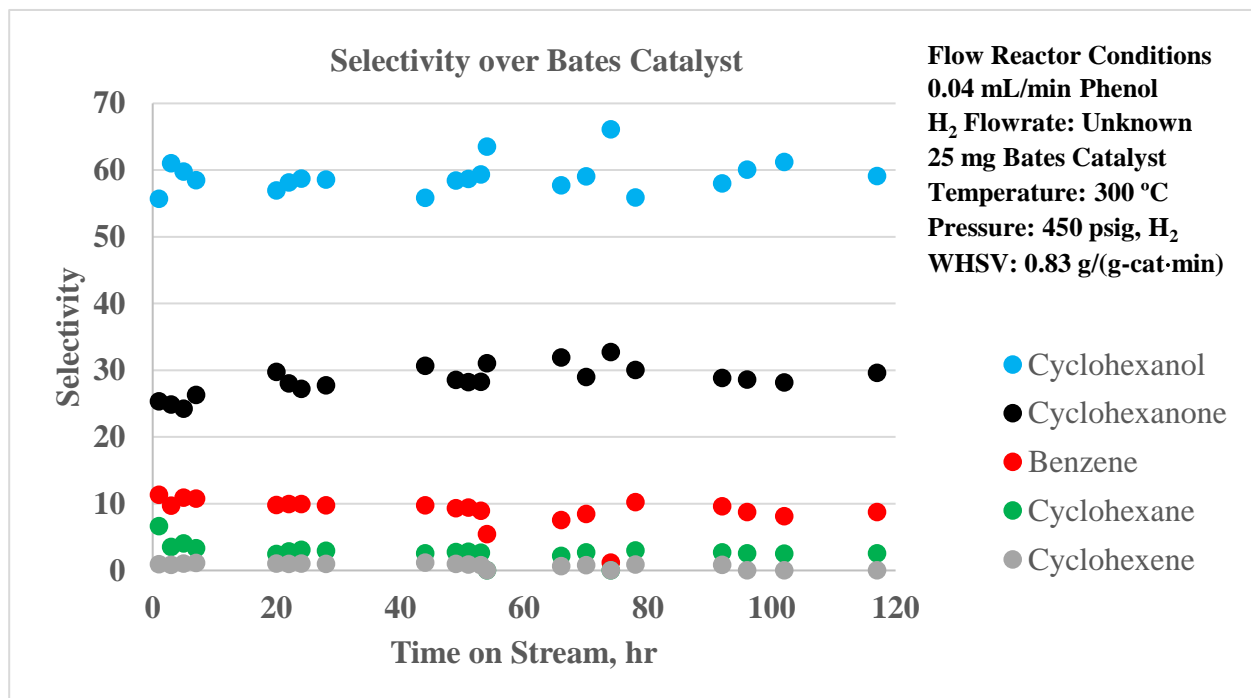
Figure 3.2 Product selectivity from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) at 1 hour sampling.

The site time yield was then calculated for both direct deoxygenation and hydrogenation pathways using Bates catalyst. The yield is calculated to test the catalytic performance for phenol HDO reaction, by dividing the total molar flow rate of products made, per moles of Ru in the catalyst. The results show that the site time yield of HYD pathway is higher than the DDO pathway. This gives an indication that the Ru/TiO$_2$ catalyst favors the HYD pathway rather than DDO pathway. It also revealed that the catalyst deactivated over time.
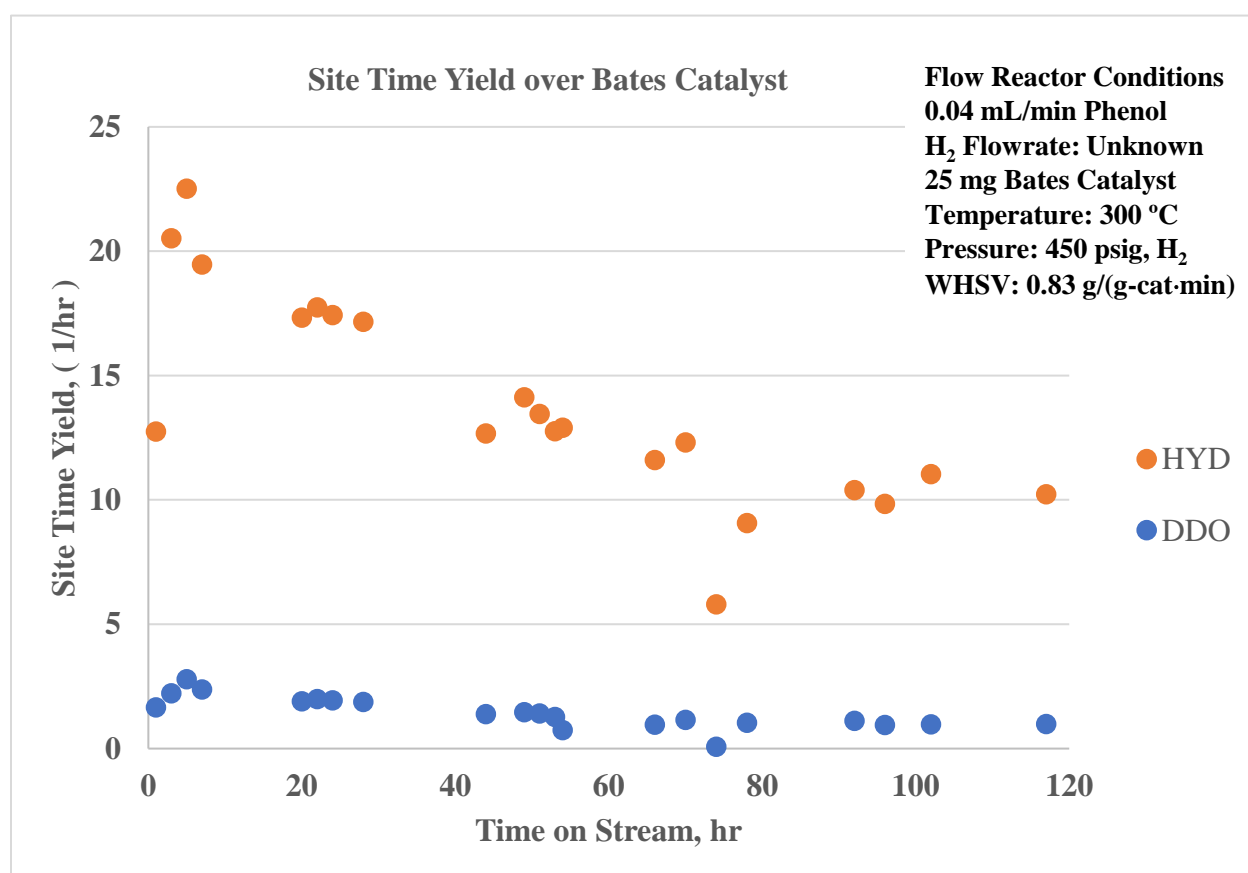
Figure 3.3 Site time yield from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) at 1 hour sampling.

Phenol conversion was also calculated for phenol HDO reaction over Ru/TiO$_2$. Figure 3.4 shows that the conversion of phenol reached ~68% and started decreasing over time to reach ~12% in 117 hours. This observation is clear evidence that the catalyst deactivated over time.
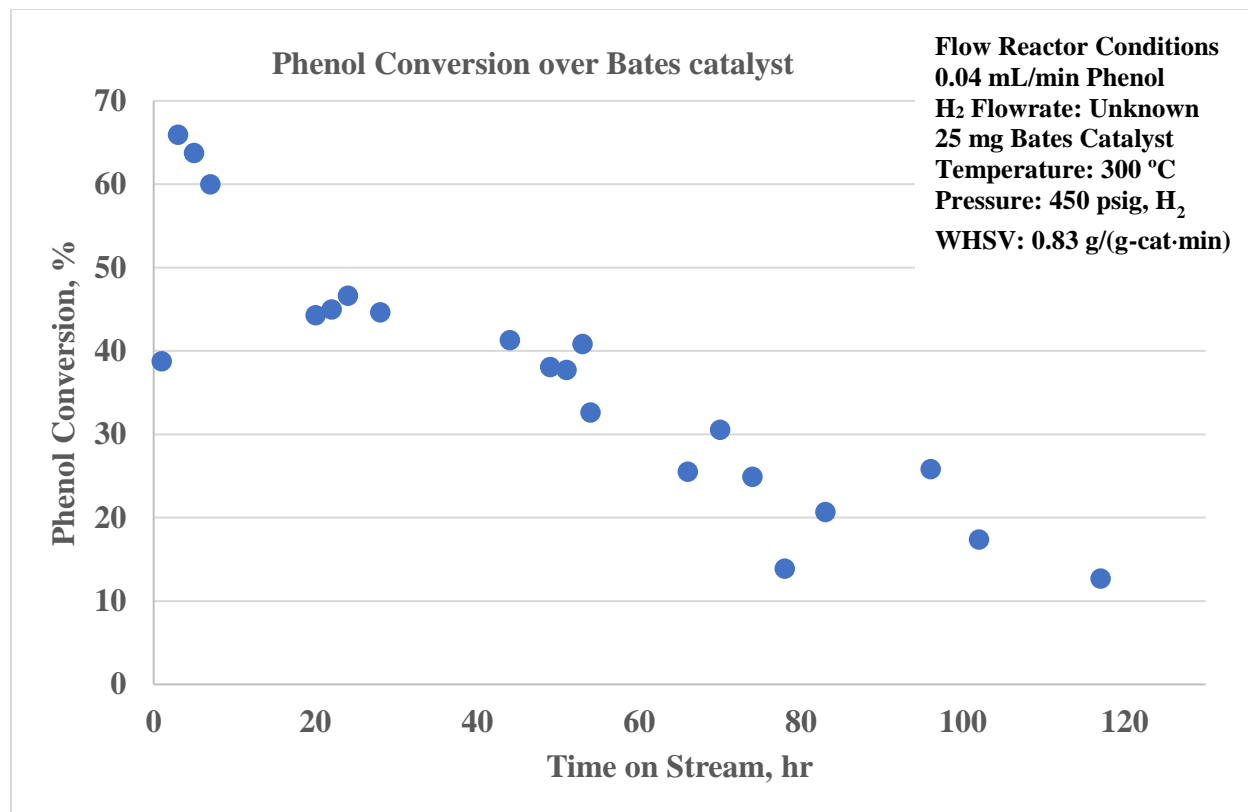
Figure 3.4 Conversion of phenol over Ru/TiO$_2$ (Bates catalyst) at 1 hour sampling.

To better understand the catalytic behaviors of Ru/TiO$_2$ in phenol HDO reaction, a newly synthesized catalyst of Ru/TiO$_2$ (UMaine catalyst) was tested under the same reaction conditions and its results are as follows:

Table 3.2 Product distribution of phenol HDO reaction over Ru/TiO$_2$ (UMaine catalyst) at 1 hour sampling

Time on Stream hr.	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol	% Cyclohexanone	% Conversion	% Deoxygenation	DDO / HYD
1	3.82	0.71	0.30	5.96	5.55	16.34	4.83	0.30
3	2.80	0.51	0.12	4.36	4.85	12.64	3.43	0.29
5	2.52	0.44	0.22	3.62	3.97	10.78	3.18	0.31
6	2.21	0.44	0.13	3.08	3.67	9.52	2.78	0.30
7	2.07	0.41	0.11	2.67	3.41	8.68	2.60	0.31
8	2.47	0.33	0.10	2.00	3.11	8.01	2.90	0.45
10	2.23	0.21	0.09	1.17	2.62	6.32	2.53	0.55
23.5	1.22	0.04	0.05	1.23	1.16	3.71	1.31	0.49
24.5	1.29	0.14	0.03	1.39	1.06	3.91	1.46	0.49
26	1.18	0.12	0.05	1.39	1.01	3.75	1.35	0.46
27	0.81	0.00	0.00	0.71	0.59	2.11	0.81	0.62
30	0.91	0.00	0.00	0.77	0.67	2.35	0.91	0.63
34	0.67	0.00	0.00	0.40	0.47	1.55	0.67	0.77
48	0.63	0.00	0.00	0.42	0.69	1.74	0.63	0.57
51	0.65	0.00	0.00	1.09	0.55	2.28	0.65	0.40
53	0.59	0.00	0.00	0.87	0.49	1.95	0.59	0.43
56	0.53	0.00	0.00	0.68	0.43	1.64	0.53	0.48
58	0.54	0.00	0.00	0.77	0.42	1.72	0.54	0.45
72	0.45	0.00	0.00	0.84	0.42	1.71	0.45	0.36
73	0.47	0.00	0.00	0.84	0.38	1.68	0.47	0.39
77	0.41	0.00	0.00	0.80	0.37	1.58	0.41	0.35
80	0.41	0.00	0.00	0.71	0.31	1.43	0.41	0.39
82	0.38	0.00	0.00	0.61	0.30	1.28	0.38	0.42
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 3.2 confirms poor activity of Ru/TiO$_2$ catalyst. It shows low selectivity towards DDO pathway, ratio of both deoxygenation products and DDO: HYD. It can be seen that the catalyst is completely dead in about 100 hours.

Figure 3.5 shows the selectivity of phenol HDO over Ru/TiO$_2$ catalyst synthesized at UMaine. It shows that the selectivity of HYD pathway is more dominant than the DDO pathway, as well as, the activity of Ru/TiO$_2$ catalyst was deactivated over time, which is consistent with the catalyst that was synthesized by our catalyst group.

Figure 3.5 Product selectivity from the HDO reaction of phenol over Ru/TiO$_2$ (UMaine catalyst) at 1 hour sampling.

The site time yield of phenol HDO reaction was also calculated over UMaine catalyst to check its activity towards DDO pathway and compare it with Bates catalyst. The results were consentient with Bates catalyst, on which HYD pathway was the dominant pathway, as well as, the activity of the catalyst was decreased over time.
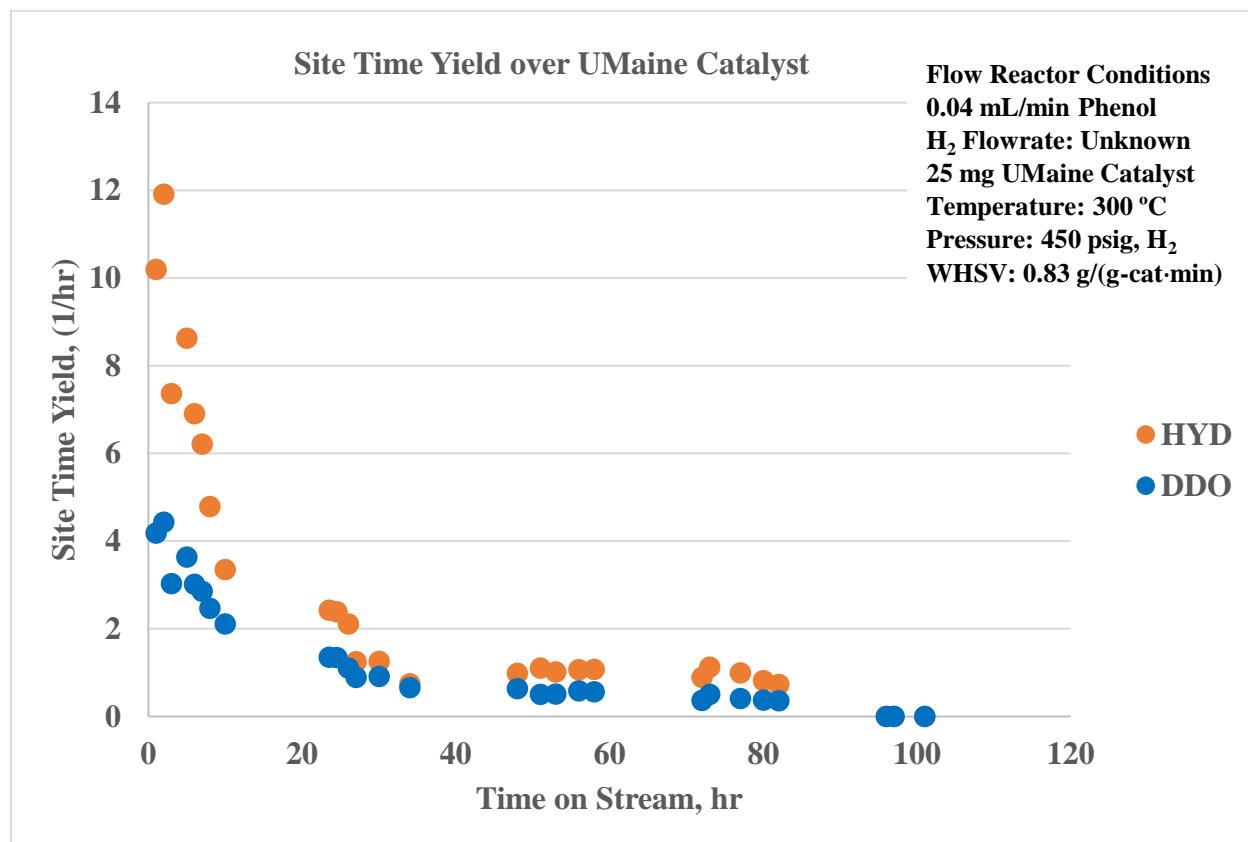
Figure 3.6 Site time yield from the HDO reaction of phenol HDO over Ru/TiO$_2$ (UMaine catalyst) at 1 hour sampling.

Phenol conversion was also calculated for phenol HDO reaction over Ru/TiO$_2$ catalyst synthesized in UMaine. Figure 3.7 shows that the conversion of phenol over UMaine catalyst was less than Bates catalyst, on which the conversion reached ~17% compared with Bates catalyst which reached ~68%. It also showed that the catalyst was completely dead at ~100 hour. This observation is also confirmed that the catalyst was deactivated over time.

31
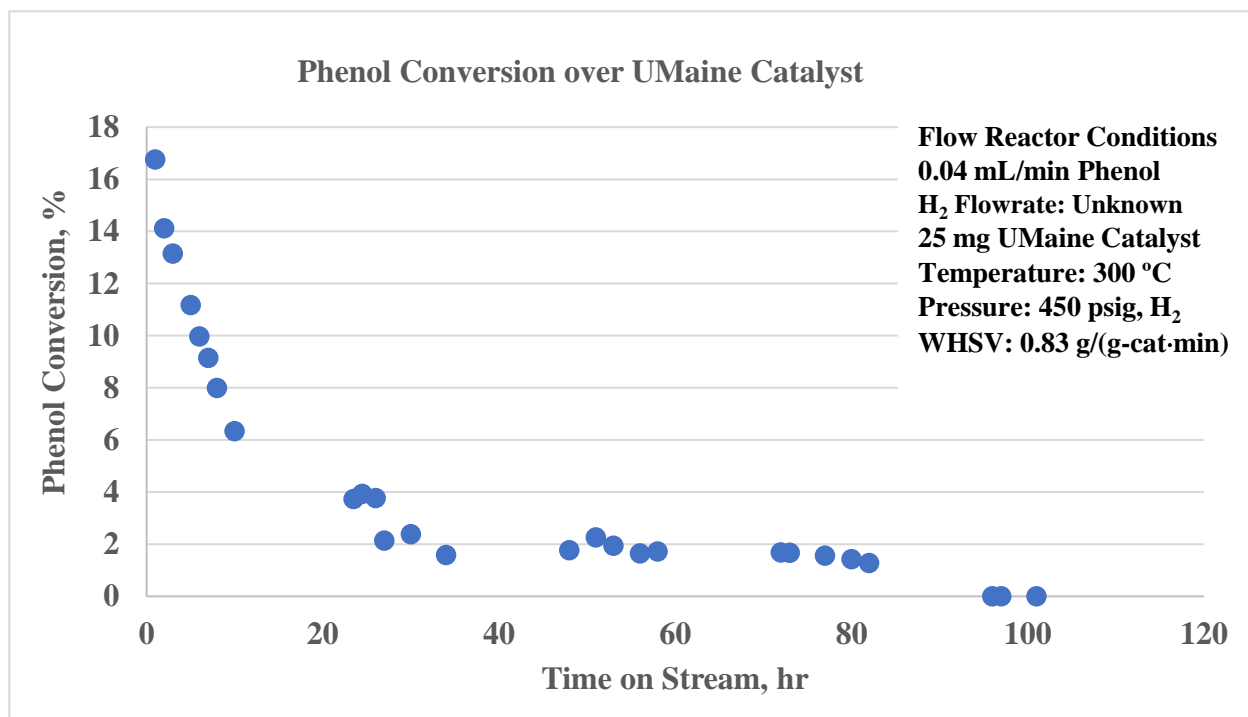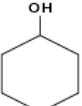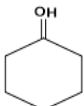
Figure 3.7 Conversion of phenol the over Ru/TiO$_2$ catalyst (UMaine catalyst) at 1 hour sampling.

Reactions were conducted in the flow reactor using a WHSV = 2.22 g/(g-cat·min) which is equivalent to the 15 minutes batch experiment results in figure 2.8. The results presented in Table 3.3 and figure 3.8 show that changing the space velocity enhanced the DDO activity of Ru/TiO$_2$ catalyst, on which benzene was the major product compared with the previous reactions which showed that cyclohexanol and cyclohexanone were the major products. It also showed that the ratio of DDO: HYD is higher than the reactions with WHSV = 0.83 g/(g-cat·min) in figure 2.7.

Table 3.3 Product distribution of phenol HDO reaction over Ru/TiO$_2$ (Bates catalyst) at 15 minutes sampling.

Time on Stream hr.	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol OH	% Cyclohexanone OH	% Conversion	% Deoxygenation	DDO / HYD
0.25	4.26	0.00	0.00	1.47	3.31	9.04	4.26	0.89
0.50	3.68	0.00	0.10	1.25	3.19	8.22	3.78	0.81
0.75	3.08	0.00	0.10	0.90	2.82	6.89	3.17	0.81
1.00	2.84	0.00	0.12	0.86	2.63	6.44	2.96	0.79
1.25	2.54	0.00	0.11	0.71	2.45	5.80	2.64	0.78
1.50	2.73	0.00	0.15	0.88	2.58	6.34	2.88	0.76
1.75	2.25	0.00	0.10	0.55	2.14	5.04	2.35	0.81
2.00	2.10	0.00	0.10	0.47	2.01	4.68	2.20	0.82
2.50	2.02	0.00	0.00	0.47	2.01	4.49	2.02	0.82
3.00	1.58	0.00	0.00	0.36	1.78	3.72	1.58	0.74

The results in figure 3.8 show that the selectivity of benzene was higher than the selectivity of the other compounds. It also showed high selectivity towards the HYD products. Based on these observations, we can conclude that the activity of Ru/TiO$_2$ catalyst was enhanced by changing the space velocity to get more selectivity towards benzene, compared with the previous experiments which were run for 1 hour.
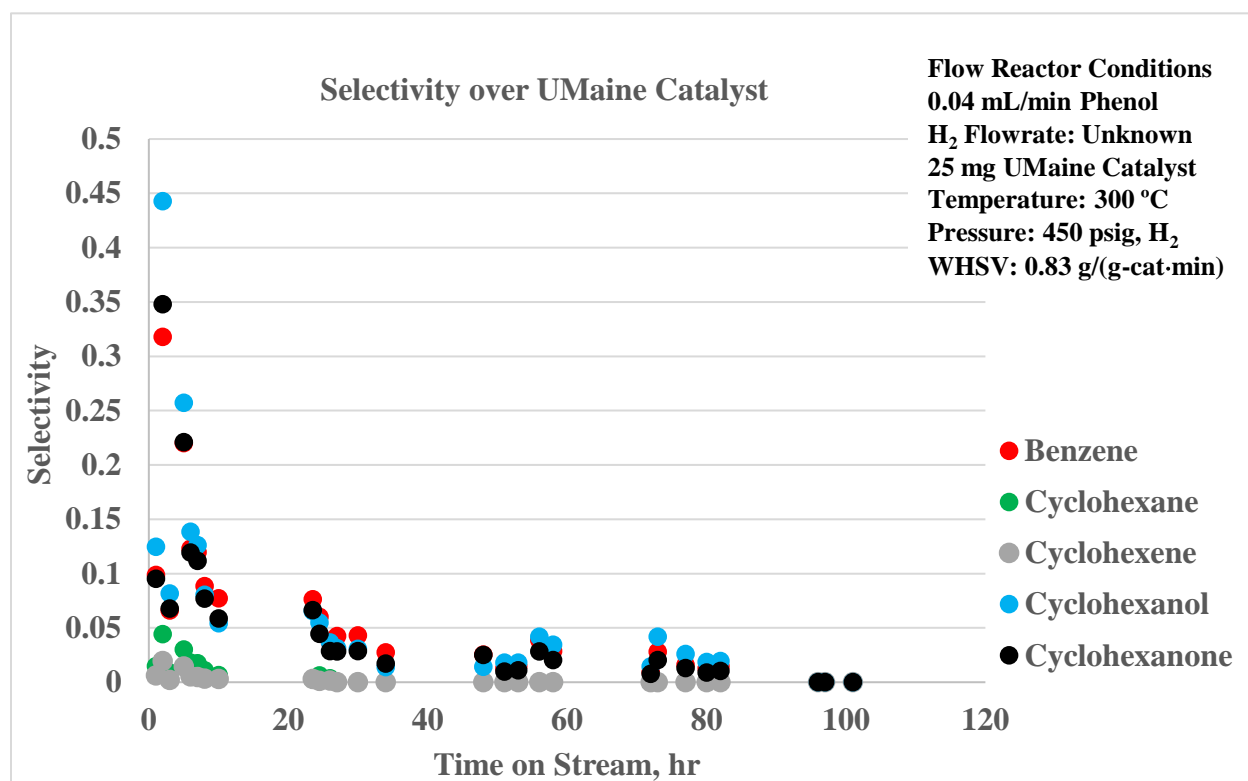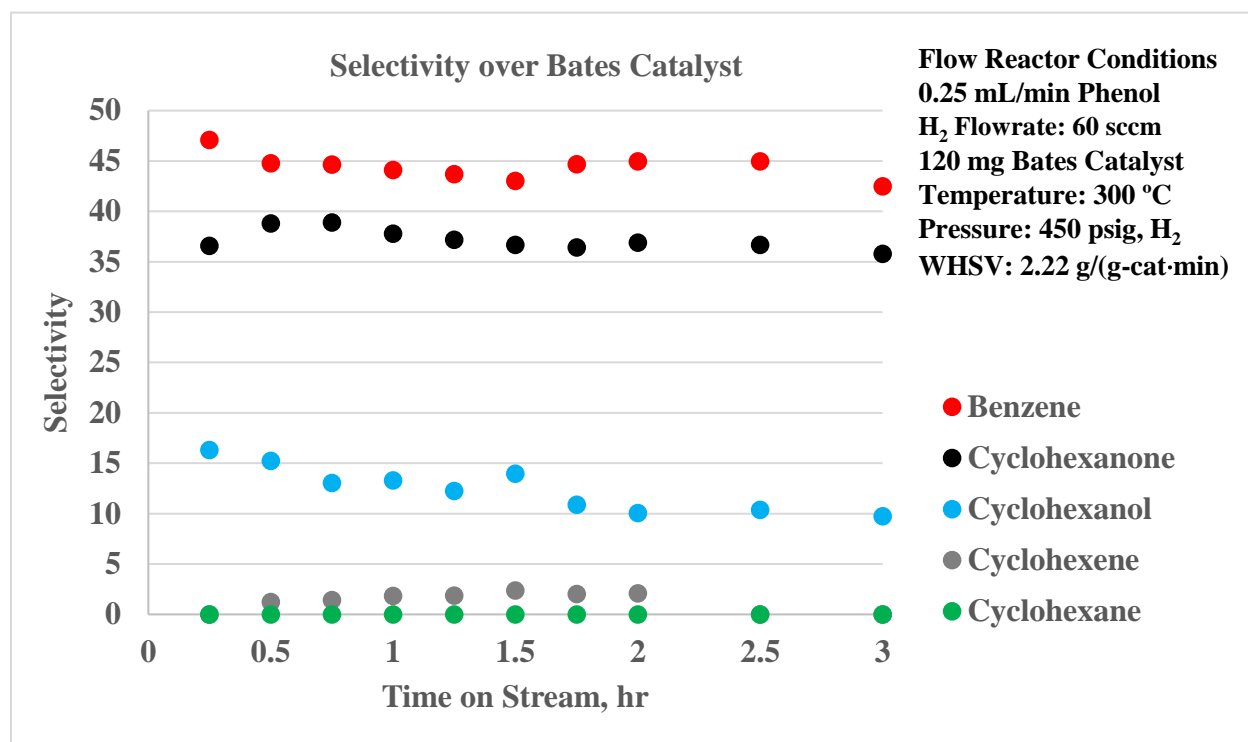
Figure 3.8 Product selectivity from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) at 15 minutes sampling.

The site time yield was then calculated to determine whether DDO pathway was the dominant mechanism. Figure 3.9 shows the site time yield of phenol HDO reaction for both DDO and HYD pathways. The results show that the site time yield of HYD products was higher than the site time yield of DDO products. This behavior is expected because the reaction showed high selectivity towards the HYD products. It is important to point out that, the site time yield of the DDO pathway became closer to the HYD pathway, after changing the space velocity to 15 minutes instead of 1 hour. This observation clearly indicates that the composition of phenol hydrodeoxygenation reaction changed by changing the space velocity.
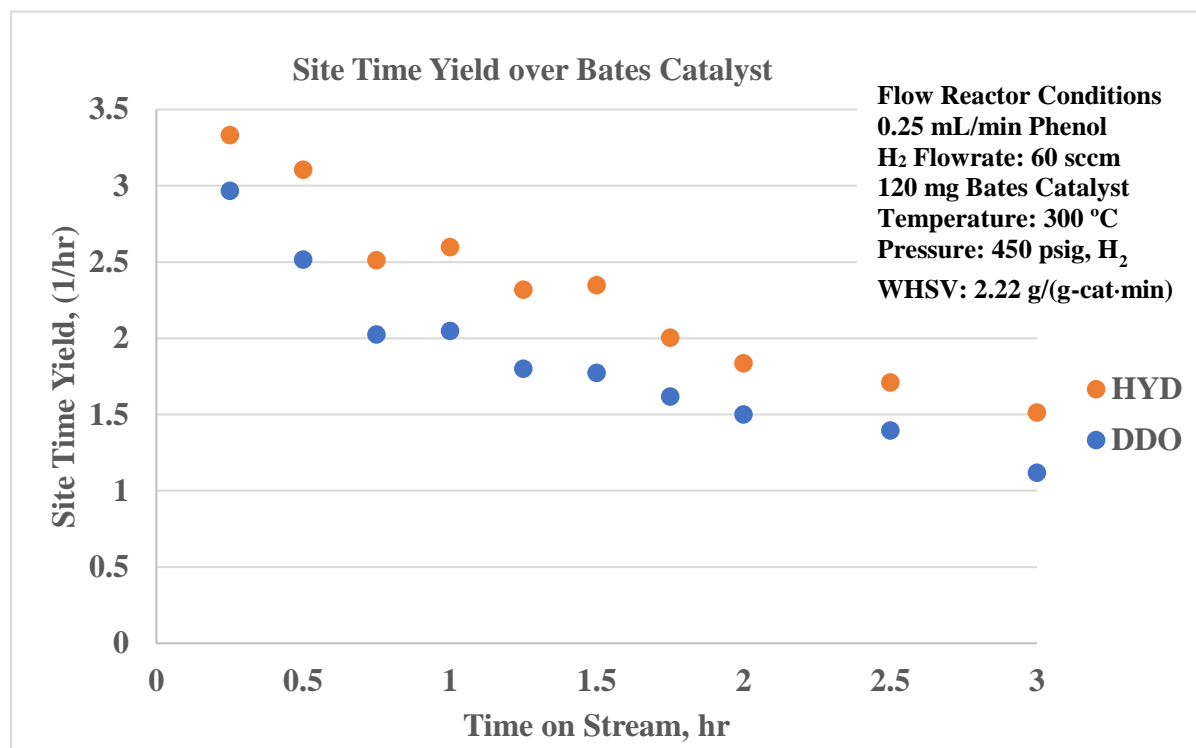
Figure 3.9 Site time yield from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) at 15 minutes sampling.

The conversion of phenol presented in figure 3.10 shows that the conversion of phenol was approximately 9% initially and started decreasing over the time to reach approximately 3.8% during 3 hours of operation. This result clearly indicates that the Ru/TiO$_2$ catalyst was deactivated over the time of reaction.

Phenol Conversion over Bates Catalyst

Flow Reactor Conditions
0.25 mL/min Phenol
H_2 Flowrate: 60 sccm
120 mg Bates Catalyst
Temperature: 300 ºC
Pressure: 450 psig, H_2
WHSV: 2.22 g/(g-cat·min)
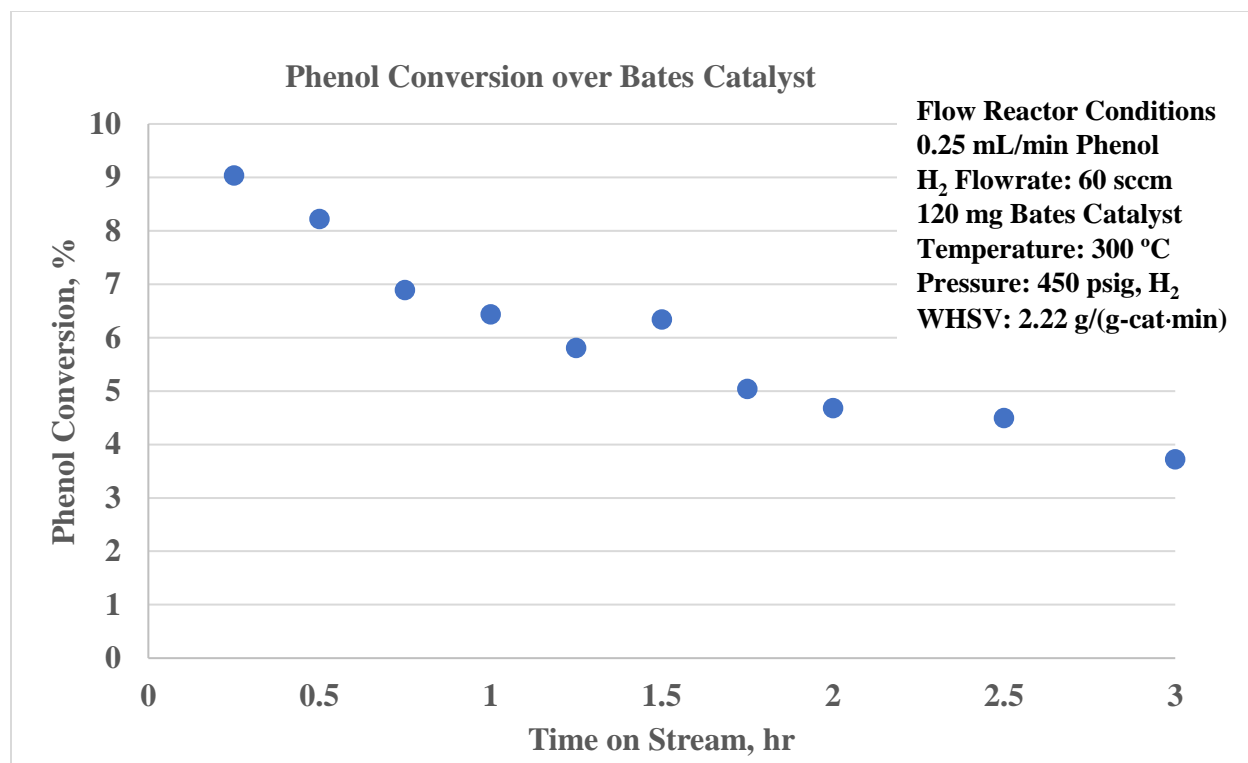
Figure 3.10 Conversion of phenol over Ru/TiO_2 catalyst (Bates catalyst) at 15 minutes sampling.

3.5.1 Effect of Solvent on Phenol HDO Reaction

It was postulated that competitive adsorption of reaction products might have been contributing to the deactivation of the catalyst. Therefore, the catalytic activity and reaction selectivity was studied for a dilute mixture of phenol using Tetrahydrofuran (THF) as a solvent. Tetrahydrofuran [$(CH_2)_3CH_2O$, 96%] was used along with 2% deionized water and 2% liquified phenol in the phenol HDO reaction, using the same reaction conditions as previously explored. However, the liquid samples were collected in this case every 15 minutes. The purpose of using a THF solvent in the phenol HDO reaction was to study its effects on the reaction selectivity and mechanism, especially, if it caused differences. The experiments then showed that the THF

solvent appears to play a role in enhancing the activity of Ru/TiO$_2$ catalyst to give a different performance in terms of activity and selectivity. This can be attributed to the dilute concentration of phenol which enhance the DDO pathway.

Table 3.4 Product distribution of phenol HDO reaction over Ru/TiO$_2$ (Bates catalyst) using THF solvent at 15 minutes sampling

Time on Stream hr.	% Benzene	% Cyclohexane	% Cyclohexene	% Cyclohexanol OH	% Cyclohexanone OH	% Conversion	% Deoxygenation	DDO / HYD
0.25	31.14	0.96	0.77	11.97	7.69	52.53	32.87	1.46
0.5	28.80	0.86	0.66	11.50	7.60	49.41	30.32	1.40
0.75	28.70	0.75	0.71	11.45	7.89	49.50	30.17	1.38
1	26.58	0.75	0.76	10.82	7.69	46.60	28.10	1.33
1.25	24.60	0.61	0.67	10.24	7.43	43.55	25.88	1.30
1.5	24.65	0.70	0.78	10.46	7.52	44.11	26.13	1.27
1.75	24.02	0.58	0.61	9.63	7.33	42.18	25.22	1.32
2	21.70	0.48	0.73	8.68	6.85	38.43	22.91	1.30
2.25	21.10	0.54	0.66	8.35	6.79	37.45	22.31	1.29
2.5	21.71	0.65	0.84	8.46	6.82	38.48	23.20	1.29
2.75	20.58	0.52	0.62	7.94	6.60	36.26	21.72	1.31

In this experiment, the results revealed that the organic solvent (THF) provide a significant enhancement in the activity of Ru/TiO$_2$ catalyst. Table 3.4 shows clear improvements in terms of yield, conversion, and the ratio of both deoxygenation products and DDO: HYD. With regards to the benzene yield, the results of previous experiments showed low yield towards benzene ~3.9%. In contrast, this experiment showed high yield towards benzene ~31.14%.

Additionally, the previous results showed low ratio of DDO: HYD less than 1.0%. However, this experiment showed high ratio of DDO: HYD ~1.3%.
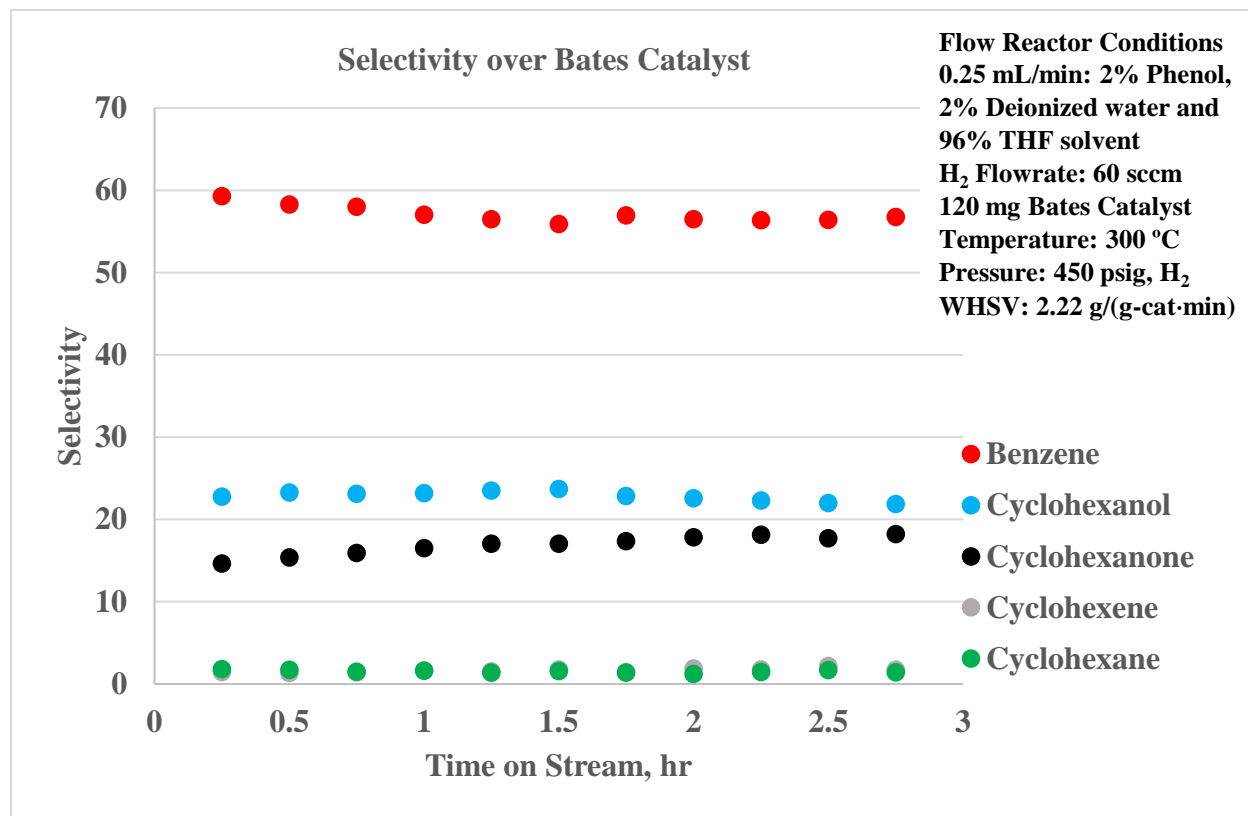
Figure 3.11 Product selectivity from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) using THF solvent at 15 minutes sampling.

Figure 3.11 presents the selectivity of Ru/TiO$_2$ catalyst using THF solvent at favored reaction conditions. The results show that THF solvent has a positive effect on the reaction, on which it leads to high selectivity towards DDO pathway (~58% benzene) compared to the results of previous experiments which gave poor selectivity towards benzene ~10%.

To examine the activity of Ru/TiO$_2$ catalyst, the site time yield was calculated to get more insight about the effect of THF solvent on the phenol HDO reaction. Figure 3.12 shows

38

that the THF solvent enhanced the activity of Ru/TiO$_2$ catalyst by getting high activity and selectivity towards DDO pathway.
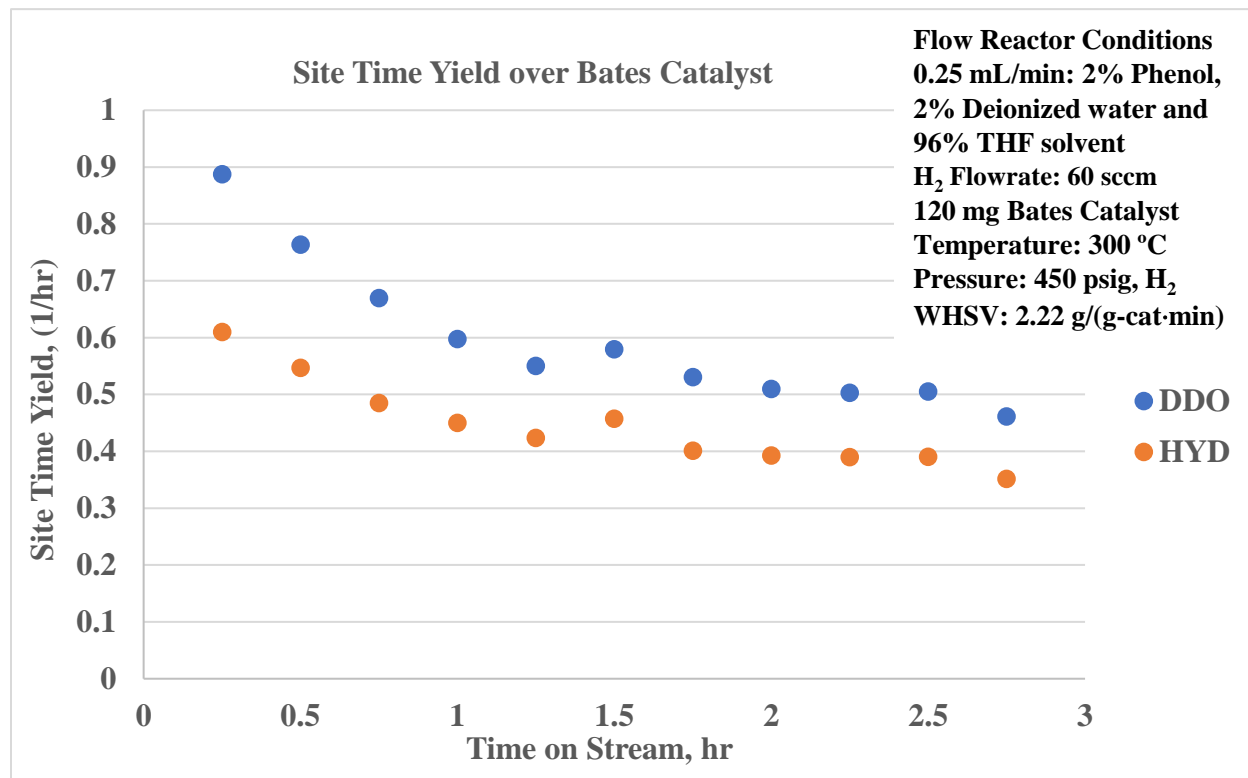
Figure 3.12 Site time yield from the HDO reaction of phenol over Ru/TiO$_2$ (Bates catalyst) using THF solvent at 15 minutes sampling.

For this reaction, conversion of phenol was also calculated and showed that the catalyst was not stable. Figure 3.13 shows that the conversion of phenol reached ~52% and started to decrease to reach ~36% at 3 hours. This observation clearly confirms that the catalyst was deactivated over time.

According to these results, it seems that the pure phenol inhibits the activity of Ru/TiO$_2$ catalyst to yield low selectivity towards DDO pathway. In contrast, diluted phenol yields high

selectivity towards benzene. These findings are in good accord with the results of the batch reactor.
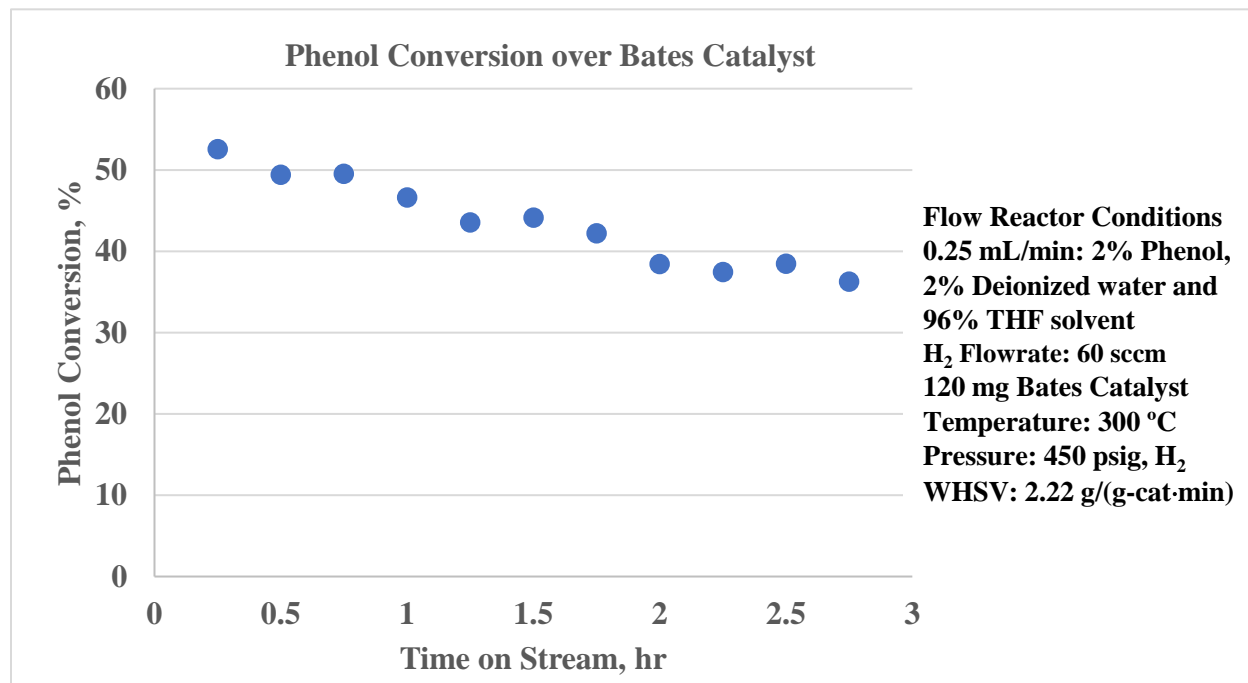
Figure 3.13 Conversion of phenol over Ru/TiO$_2$ catalyst (Bates catalyst) using THF at 15 minutes sampling.
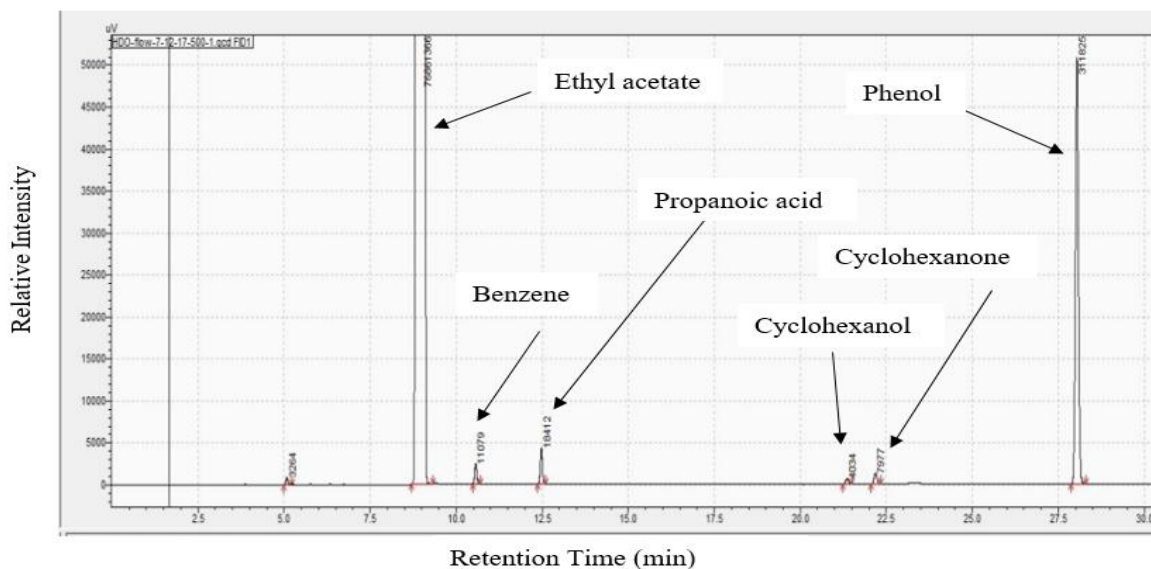
Figure 3.14 GC-FID chromatogram of phenol HDO products over Ru/TiO$_2$ (Bates catalyst) at 1 hour sampling.

40

The selectivity of phenol HDO products observed in the batch reactor over Ru/TiO_2 catalyst synthesized at Bates for 1 hour of reaction time, showed that benzene was the major product, followed by cyclohexanol and cyclohexanone. In contrast, the selectivity of phenol HDO reaction over UMaine catalyst at same reaction time showed that benzene was the major product followed by cyclohexane.

Additionally, the selectivity of phenol HDO products reached over the Bates catalyst at 15 minutes of reaction time, showed that benzene was the major product in three experiments followed by cyclohexanol and cyclohexanone. Whereas, the selectivity of benzene, cyclohexanol, and cyclohexanone were almost equal for the two other experiments at the same reaction time.

By correlating these observations to the hydrogenation mechanism, it is very obvious that the Ru/TiO_2 catalyst synthesized at Bates, gives high selectivity towards cyclohexanol and cyclohexanone for both times of reaction. In contrast, the Ru/TiO_2 catalyst synthesized at UMaine, provides high selectivity towards cyclohexane.

CHAPTER 4

MECHANISMS OF CATALYST DEACTIVATION

Based on the data collected in both the batch and flow reactors, the Ru/TiO$_2$ catalyst showed deactivation during the progress of the reaction. Actually, I have not tested the catalyst after reaction to figure out the reason that made it deactivate. Therefore, I suppose three possible mechanisms for catalyst's deactivation. The first mechanism is called coke formation, this kind of deactivation is caused by the thermal instability and it happens when the carbonaceous material is covering the active sites on the surface of the catalyst and blocking the catalyst's pores. The coke formation can be analyzed by TGA method (Thermogravimetric analysis).

The second mechanism is called, metal sintering, this kind of deactivation is caused by the high temperature of reaction. It leads to decreased interfacial sites between the metal particles and the support. For this kind of deactivation, transmission electron microscopy (TEM) technique can be used to test the catalytic sintering.

A third mechanism, is called losing of active metal catalyst. This kind of deactivation is caused by leaching the active metal of catalyst into the liquid phase. ICP analysis method can be used to test the leaching of active site metal, by dissolving and analyzing the used catalyst.

The three above mechanisms seem to have an effect on the hydrogenation mechanism, on which coke formation blocks the active site of small metals, and has much stronger effect than metals, the sintering metals favors the HYD products rather than DDO product. This observation was related to our catalyst group base on their previous data [5]. Finally, leaching metals also leads to HYD pathway where the interfacial site between the small particles of catalyst and the support will be decreased.

CONCLUSION

In this work, Ru/TiO$_2$ catalysts were synthesized at Bates and UMaine, they were then used in batch and flow reactors. The performance of Ru/TiO$_2$ catalyst in the batch reactor is better than its performance in the flow reactor. The batch reactor results show high activity and product selectivity for phenol DDO, as compared to the flow rector.

The data collected using the batch reactor, along with both the "Bates" and "UMaine" catalysts, are consistent with previous data from our catalyst group which used the same reactor set up. In contrast, the data collected using the flow reactor, with each catalyst, shows much lower ratio of DDO: HYD, than what was previously understood for this catalyst in the batch reactor. It should be noted that the activity, selectivity, and stability of Ru/TiO$_2$ catalyst were not stable at same reaction conditions.

In the batch reactor, the main product was benzene, however, a large amount of cyclohexanone and cyclohexanol was detected in the flow reactor. These observations demonstrate that the selectivity of phenol HDO reaction was different in each reactor.

The use of the organic solvent Tetrahydrofuran (THF) in flow reactor helps to enhance the activity of Ru/TiO$_2$ catalyst and showed an improvement towards the formation of benzene (DDO pathway). It gave higher ratio of DDO: HYD, which is consistent with the batch reactor results. In both reactors, the catalyst showed deactivation during the progress of the reaction. The flow reactor never achieved steady state, while running in excess of 120 hours, while the batch reactor was only operated for 1 hour at an equivalent space velocity (time). These results demonstrate that the selectivity for HDO of phenol can be controlled by using an organic solvent.

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APPENDIX A

APPENDIX A STANDARD OPERATION PROCEDURE FOR EXPERIMENTS PERFORMED

A.1 Standard Operating Procedure for 25 mL Parr Reactor (Batch Reactor)
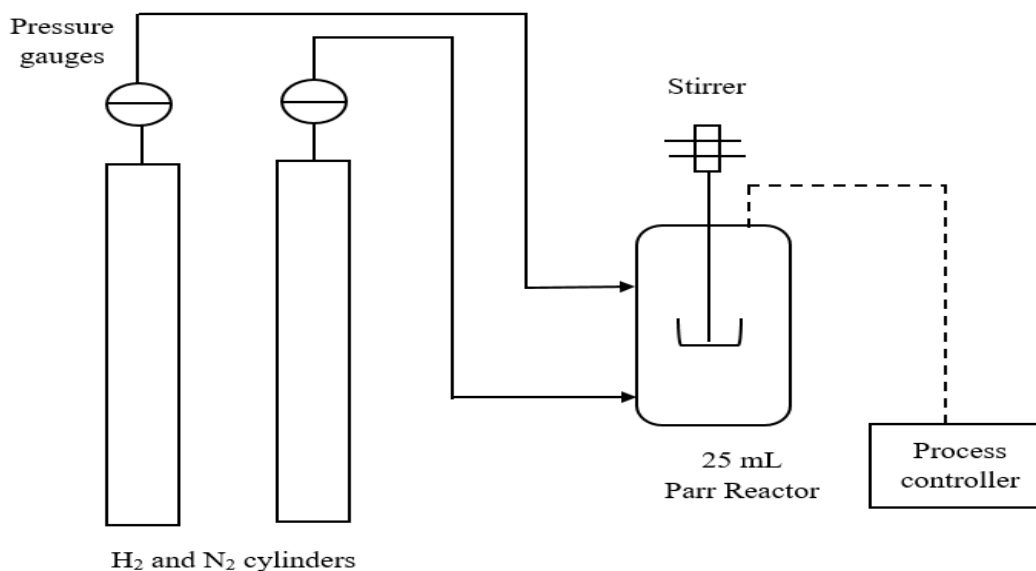
1. Start hood, turn ON computer and process controller.

2. Charge the catalyst into the reactor and attach the reactor vessel to the head.

3. Seal reactor vessel first using collar clips, followed by wrench tightening.

4. Turn on the cooling water for the stirrer.

5. Set the pressure on the H_2 regulator to 125 psig. Open the main valve on the hydrogen cylinder.

6. Open the outlet valve on the reactor and vent it to a bubbler.

7. Carefully open the inlet valve on the reactor. Monitor the gas flow from the reactor to ensure a steady flow of gas coming out of the reactor.

8. Heat the reactor to the desired temperature 300 °C.

9. Once temperature stabilized, leave the catalyst at desired temperature under flowing gas for half hour.

10. Close the outlet valve on the reactor and open the inlet valve on the reactor and allow the system to reach desired reduction pressure (550 psig).

11. Allow the pretreatment reaction to run for one hour under static atmosphere.

12. Cool the reactor to room temperature and then slowly open the outlet valve to release the hydrogen.

13. Purge the reactor with 40 psig nitrogen three times.

14. Open the reactor vessel, add 5 mL of liquefied phenol into the pretreated catalyst, minimize the amount of time that the catalyst is exposed to air after being pretreated, and attach the reactor vessel to the head.

15. Purge the reactor again with 40 psig nitrogen three times to remove oxygen from the vessel.

16. Pressurize the reactor one final time with nitrogen to a final pressure of around 15-20 psig.

17. Set the stirring speed to 750 rpm.

18. Heat the reactor to the desired temperature 300 °C.

19. Once temperature stabilized, slowly open the H_2 inlet valve on the reactor until the final pressure is achieved. (550 psig of H_2 + partial pressure of nitrogen in the reactor).

20. Allow the reaction to run for 1 hour.

21. After reaction, cool the reactor to the room temperature.

22. Collect and store products in glassware labeled with date, chemical identification, owner, and hazards.

23. Clean reactor and shut off hood.

A.2 Standard Operating Procedure for Flow Reactor (Packed Bed Reactor)
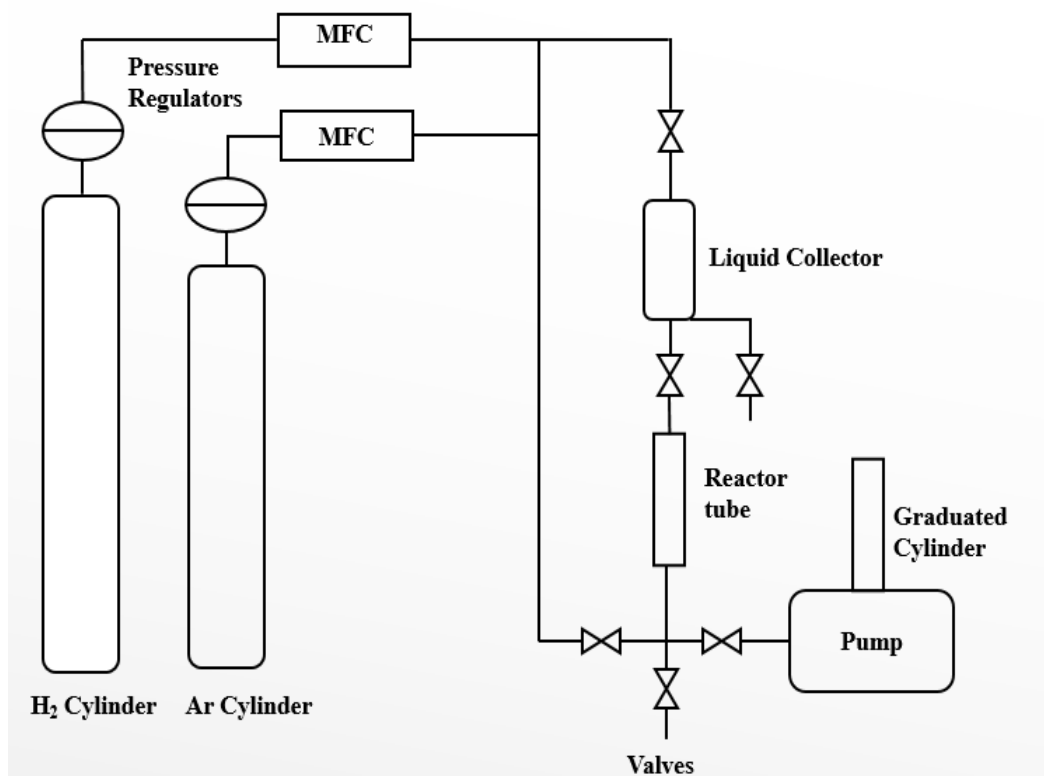
1. Cut 6 inches of ¼" tubing as reactor tube.

2. Weigh 25 mg of Ru/TiO_2 catalyst required for the experiment.

3. Weigh ten-times as much crushed fused silica.

4. Mix the silica and catalyst in a vial.

5. Pack a plug of quartz wool inside the ¼" tubing. On the outside of the tubing mark the position of the quartz wool plug.

6. Fill the dead volume below this plug with fused silica chips and secure with a second plug of quartz wool at the end of the tubing.

7. Load the mixture of catalyst and silica into the reactor.

8. Pack a second plug of quartz wool up to the catalyst.

9. Fill the dead volume up this plug with fused silica chips and secure with a second plug of quartz wool at the end of the tubing.

10. Connect the packed ¼" tubing to the reactor system and seal it.

11. Verify that the correct safety relief valve is connected to the reactor.

12. Slowly pressurize the system to the reaction pressure (450 psig) with H_2 and check that all connections are leak-tight using soapy water. Pressurize the reactor simultaneously from the top and bottom to avoid moving the catalyst bed.

13. Verify that the main thermocouple and fail-safe thermocouple are connected to the temperature controller.

14. Position the main thermocouple inside the heat transfer blocks and make sure its tip touching the reactor tube. Place the tip of the fail-safe thermocouple inside the heat transfer blocks. Wrap a heating tape around the blocks; cover the heating tape with insulation; and hold the insulation in place with foil.

15. Connect the reactor heating tape to the Variac that is connected to the temperature controller.

16. Set the mass flow controller to the appropriate flowrate (30 sccm) with H_2 and pressurize the reactor to the reaction pressure.

17. Set the temperature controller on Address 1 to the Control Mode "Ramp/Soak" and Edit the Ramp/Soak Pattern as needed for the reaction.

18. Start the temperature controller. Let the reactor heat up under flowing H_2 for reducing the catalyst and preparing for reaction.

19. Once temperature stabilized, set the HPLC pump to the appropriate flowrate (0.04 mL/min), and pump against the closed 1-way valve until the pressure rises above the reaction pressure. While pumping, open the 1-way valve and start the stopwatch.

20. When ready to sample, record the pressures and the amount of liquid feed left in the graduated cylinder, close the liquid and both up and down valves of reactor leaving both the MFC and HPLC pump running.

21. Verify the needle valve is closed, and open the ball valve on the separator drain line.

22. Slowly, open the needle valve to collect the sample out of separator.

23. Re-pressurize the separator using the valve at the top of the separator. Open the inlet and outlet valves of reactor, then open the liquid valve.

24. Close the liquid shut-off valve and switch off the HPLC pump.

25. Switch from H_2 to Ar.

26. Turn off the Variac and let the system cool under Ar flow.

27. Once cool, de-pressurize the system by bypassing the backpressure regulator.

APPENDIX B

GC-FID METHOD FOR PRODUCT ANALYSIS

B.1 GC-FID Program for Analyzing Samples

GC-FID program for analyzing samples from phenol hydrodeoxygenation

- GC make (model): Shimadzu (GC-2010)

- Column type: Agilent J&W GC Column

- Ethyl acetate was used to dilute the samples prior injection

- Column Oven Temperature Program:

1. Start at 40 °C and hold for 1 min

2. Ramp from 40 °C to 120 °C at 5 °C/min

3. Hold at 120 °C for 2 min

4. Ramp from 120 °C to 180 °C at 5 °C/min

5. Hold at 180 °C for 2 min

6. Ramp from 180 °C to 250 °C at 25 °C/min

7. Hold at 250 °C for 2 min

- Injector Port: 260 °C with 20:0 split ratio

- Carrier Gas: Helium

- Ion Source Temperature: 400 °C

B.2 Pre-Analytical Checklist and PPE

1. Required PPE (goggles, nitrile gloves, lab coat).

2. Micropipettes and pipette tips.

3. Syringe and filter.

4. 2 mL vials for analytical chromatography and caps.

5. Phenol HDO (Products) and Ethyl Acetate (Solvent).

B.3 Preparation of Phenol HDO Standards

Add 0.95 mL of phenol HDO products (Benzene, Cyclohexane, Cyclohexene, Cyclohexanol, and Cyclohexanone) to 100 mL volumetric flask.

1- Fill the volumetric flask to the 100 mL line with ethyl acetate (Stock Solution).

2- Shake to mix well and make serial dilutions of stock as follows:

- Add 1 mL of stock solution to 10 mL total (1 mL stock + 9 mL Ethyl Acetate)

- Add 0.8 mL of stock solution to 10 mL total (0.8 mL stock + 9.2 mL Ethyl Acetate)

- Add 0.6 mL of stock solution to 10 mL total (0.8 mL stock + 9.4 mL Ethyl Acetate)

- Add 0.4 mL of stock solution to 10 mL total (0.4 mL stock + 9.6 mL Ethyl Acetate)

- Add 0.2 mL of stock solution to 10 mL total (0.2 mL stock + 9.8 mL Ethyl Acetate)

3- Shake to mix well and placing each solution in a 2 mL GC vial.

4- Store the residual stock solution in the freezer for subsequent analyses.

B.4 Preparation of Phenol HDO Samples

1- Add 0.1 mL of phenol HDO product in a vail and add 9.9 mL of ethyl acetate.

2- Shake to mix well and transfer the liquid into 2 mL vials.

3- Place vials on the auto-sampler.

APPENDIX C

EX-SITU REDUCTION TECHNIQUE

1. Start hood.

2. Load appropriate amount of Ru/TiO_2 catalyst into reduction cell.

3. Connect the gas tube on one side of reduction cell, plug the second side, and connect the bubble meter to the other side.

4. Place the thermocouple inside the hole of glass and make sure that its tip is touching the part of glass that is in contact with the catalyst.

5. Open the argon cylinder and then line up the valve to slowly deliver argon flow to reduction cell.

6. Leave the cell under argon for 5 minutes to remove the oxygen from the cell.

7. Open the hydrogen gas and line up the valve to deliver H_2 flow to the reduction cell and stop the argon flow.

8. Get appropriate flowrate of H_2 (20 sccm).

9. Place the reduction cell inside the heater and make sure that it is not touching the heater's wall.

10. Set the temperature controller as follows:

    10.1 Ramp the temperature from 20 °C to 25 °C for 5 minutes

    10.2 Ramp the temperature from 25 °C to 400 °C for 6 hours

    10.3 Hold the temperature at 400 °C for 4 hours

    10.4 Decrease the temperature from 400 °C to room temperature for 1 minute

11. At room temperature, flow argon into activated catalyst for 5 minutes.

12. Disconnect the reduction cell from gas tube.

13. Close the hydrogen and argon cylinders.

14. Leave the reduction cell for 24 hours for to slowly passivate the catalyst.

15. Store activated catalyst in glassware labeled with date, chemical identification, and owner.

16. Turn off the hood.

BIOGRAPHY OF THE AUTHOR

Abdulazeez Khlewee was born in Nasiriya, Iraq. He graduated from Southern Technical University, Basrah, in June 2007 with a Bachelor's in Petrochemical Engineering. After graduation, he worked with the Center for Engineering Studies and Designs for 4 years. He is currently employed by Thiqar Oil Company in Iraq as a production engineer where he has worked since 2011. He enrolled at the University of Maine in August 2015 in the Chemical Engineering graduate program. Abdulazeez is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in August 2017.