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**Catalytic Upgrading of Pyrolysis Oil to Transportation Fuels**

A Dissertation Presented

by

**Wei Nan**

to

The Graduate School

in Partial Fulfillment of the

Requirements

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Abstract of the Dissertation

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in

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**2014**

Increasing fossil fuel prices and the demand for clean energy have accelerated research on renewable energy sources. Pyrolysis oil (also known as bio-oil) which can be derived from lignocellulosic biomass by a fast pyrolysis process has the potential to substitute for petroleum-derived transportation fuels. However, pyrolysis oil has lower energy density (15-19 MJ/kg), compared with petroleum (40 MJ/kg) due to the high oxygen content (30-60 wt %). Furthermore, pyrolysis oil is thermally unstable that tends to age and results in phase separation at room temperature. Therefore, upgrading of pyrolysis oil is necessary before it can be used as a transportation fuel.

Hydrotreating is an effective option to upgrade pyrolysis oil to generate hydrocarbons. However, the conventional process requires elevated temperatures and pressure of H<sub>2</sub> to ensure a high level of deoxygenation. At high temperatures, coke formation by polymerization of hydroxyphenols or methoxyphenols in pyrolysis oil has been observed as the main factor affecting

the stability of the catalysts. In addition, catalytic upgrading under a high temperature increased the carbon loss to CO<sub>2</sub> and CH<sub>4</sub>. Thus, a more economical method is needed.

Our efforts to carry out hydrodeoxygenation (HDO) at relatively mild conditions to produce alcohols and hydrocarbon fuels over various supported catalysts are reported here. Different solvents have been tried to ease the problems of high viscosity and thermal instability of pyrolysis oil, clogging of reactors, considerable coking, and catalyst deactivation. The highest gas yield of HDO of pyrolysis oil was 21.1 NL/kg and the gas phase generated during upgrading had 70-85% CO<sub>2</sub>, which indicated that the oxygen in the pyrolysis oil was successfully removed. Acetic acid content decreased from 3.85 wt% to below 0.01 wt% after HDO. FT-IR data reveals that alcohols tend to be produced at lower temperatures and alkene C=C stretching vibration was found in the IR data of the upgraded pyrolysis oil showing that hydrocarbons were produced during HDO. The main products included up to 16.1% alcohols, 3.8% cyclic compounds, 21.2% hydrocarbons and 35.7% phenolics. Alcohols production can be used as gasoline additive to increase its octane number. Hydrocarbons production mainly contained C15-C16 hydrocarbons that fall in diesel carbon range. Our results successfully demonstrate a potential method for upgrading pyrolysis oil into transportation fuel under mild conditions.

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# Chapter 1: Introduction

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The need for alternative fuels has drawn a great deal of attention the world over. Numerous factors lead to increased demands for alternative fuels. Burning of fossil fuels, for instance, is known to increase the amount of greenhouse gases in the atmosphere that contribute to global warming (IPCC report, 2006). In order to satisfy environmental concerns over fossil fuel usage, many alternative fuels are being developed such as pyrolysis oil, biodiesel, bio-alcohols and other biomass sources. Economic concerns also drive the demand for alternative fuels. As production rates of traditional petroleum enter a terminal decline, rising fuel costs have become a great concern. According to the IEA report (IEA, 2011), fossil fuels will dominate the energy mix even beyond 2035. However, the need to reduce dependence on foreign oil has been the leading driving force in the U.S. toward developing and utilizing alternative fuels.

As the only renewable source than can be converted to liquid fuels, biomass is obtaining the most attention. As reported in other's study, liquid fuels can be produced from biomass via three main paths: 1) Syngas formation from gasification followed by Fischer-Tropsch process. 2) Pyrolysis and liquefaction of biomass to produce pyrolysis oil. 3) Fermentation of sugar portion to produce alcohols.[1] Among these methods, pyrolysis is considered as a very effective way of biomass conversion. Biomass such as soybean straw, corn stover and switchgrass can be converted into a liquid fuel by pyrolysis in which the biomass is thermally decomposed in the absence of oxygen at ambient pressure and a controlled temperature.[2, 3] This liquid fuel is called bio-oil or pyrolysis oil and after upgrading, it could become a promising alternative fuel. It is sustainable, renewable, and environmentally friendly as it is derived from biomass. In addition, with numerous combustion tests performed using different scale boilers, gas turbine systems, and diesel engines it has been shown that pyrolysis oil can be burned efficiently in standard or modified equipment.[4] However, before upgrading, due to its high acidity (pH: 2-3), high oxygen (35-60 wt%), and water

(15-30 wt%) contents, pyrolysis oil has lower energy density (15-19 MJ/kg) compared to petroleum (40 MJ/kg).[5] Furthermore, pyrolysis oil tends to age and phase separate at room temperature because of its instability. Pyrolysis oil is a complex mixture of over 300 organic compounds, mainly acids, alcohols, aldehydes, esters, ketones, sugars, phenols, and phenol derivatives, components with multifunctional groups, and a large proportion (20.0-30.0 wt%) of lignin. Some of these compounds are directly related to the undesirable properties of pyrolysis oil; for example, aldehydes and compounds with an unsaturated carbon bond in pyrolysis oil, are active for polymerization and condensation reactions.[6] These reactions result in increased viscosity and phase separation in the pyrolysis oil. Carboxylic acids, such as formic acid and acetic acid, make pyrolysis oil very corrosive, which imposes more requirements on construction materials of the vessels and the upgrading process before using pyrolysis oil as transport fuels.[7] The acids in pyrolysis oil also accelerate pyrolysis oil aging and the properties decline. Therefore, upgrading is necessary before pyrolysis oil can be used as a fuel in current equipment.

### **1.1.Pyrolysis**

Pyrolysis is known as a thermochemical decomposition process involving biomass heating in the absence of oxygen to carefully controlled temperatures. Under these conditions, pyrolysis gases, volatile vapors and charcoal are produced. Then, volatile products are condensed to pyrolysis oil (or bio-oil) after quickly cooling. Depending on temperature, heating rate and residence times of pyrolysis operating conditions, pyrolysis is classified as either slow or fast. The comparison of fast and slow pyrolysis is given in Table 1-1.



**Table 1- 1** Comparison of fast and slow pyrolysis process

<b>Process</b>	<b>Conditions</b>		<b>Advantages</b>	<b>Disadvantages</b>
	<b>Temperature</b>	<b>Residence time</b>		
Slow pyrolysis	Slow heat to 300-400 °C	30 minutes or more	<ul style="list-style-type: none"><li>• Small and inexpensive units</li><li>• Flexible feedstock</li><li>• High yield and high quality of biochar</li></ul>	<ul style="list-style-type: none"><li>• Difficult to scale</li></ul>
Fast pyrolysis	Fast heat to 500°C	Less than 2 seconds	<ul style="list-style-type: none"><li>• Very high yield of liquid product</li></ul>	<ul style="list-style-type: none"><li>• Feedstock must be dry and recued to less than 2 mm</li><li>• Energy balance can be a problem</li></ul>

### **1.1.1. Slow pyrolysis**

Slow pyrolysis involves slow heating rates to 300~ 400°C and held there for 30 minutes or more. Vapors can undergo subsequent reaction to form high yield and high quality of biochar, up to 35 wt%, 35 wt% of gas, 21 wt% of water and a small fraction of pyrolysis oil (9 wt%). It requires small and inexpensive units which can be set up close to feedstock supply site. Moreover, various and flexible feedstocks can be used without pretreatment. However, the low liquid products yield is not suitable for pyrolysis oil production.[8]

### **1.1.2. Fast pyrolysis**

Compared to slow pyrolysis, fast pyrolysis is performed at a higher heating rate of 1000 °C/s, to 10000 °C/s and much lower vapor residence times of a few seconds or less. The reactor provides heat for pyrolysis while maximizing heat transfer rate between media (solid or gas) and biomass particles (solid). Various reactor configurations including bubbling transport reactors, fluid beds, and cyclonic reactors) achieved high liquid oil yields of 70 - 80 % on dry biomass weight basis.

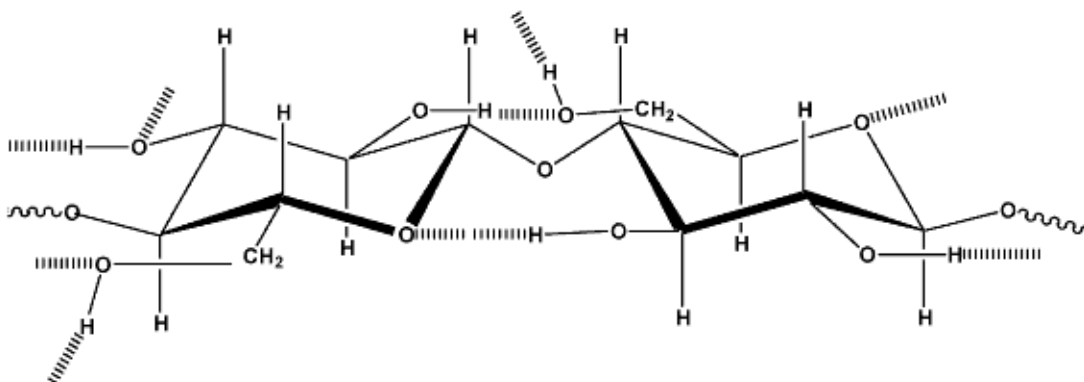
Solid char is the other product formed with a yield of 12 - 25 wt% and non-condensable gas formation reaches a yield of 13 - 25 wt% (on dry biomass weight basis). Since oil and char are collected as the value added products and gases are recycled to be combusted and provide heat for pyrolysis, no waste is produced. Over the past twenty years, fast pyrolysis of different biomass feedstocks has been widely studied to increase the yields of liquid and gaseous products to obtain valuable chemicals and fuels.[8]

High heating rates are effective to minimize char yield and maximize liquid yield at temperatures of  $\sim 500^{\circ}\text{C}$ . Further increase in temperature will increase gas yield. No char was observed under some conditions.[9] High heating rate and rapid quenching of vapors lead to formation of intermediate liquid products which immediately condense into liquid oil, thereby preventing them from being decomposed to gaseous products. At high temperatures of above  $700^{\circ}\text{C}$  and short residence times, very high gaseous product yields up to 80 wt% were observed. Intermediate products formed during pyrolysis are estimated to exceed 200 species. Model compound studies are conducted on cellulose as a dominant constituent of wood to obtain more insight into the mechanisms of decomposition during pyrolysis because it decomposes over almost the whole temperature range of fast pyrolysis.

## **1.2. Pyrolysis oil constituents**

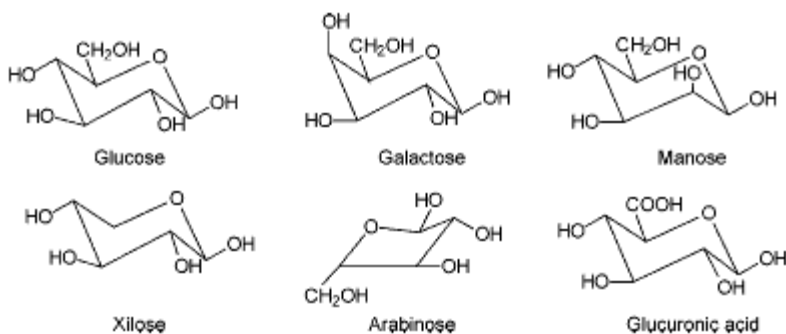
Biomass is comprised of three main structures, cellulose, hemicellulose and lignin. Cellulose is the basic constituent of wood cell walls, which provide strength for wood and account for 40~50 wt %. It is a high molecular weight (exceeding  $10^6$ ) polymer. The  $\beta$ -linked glucopyranose units of cellulose are fully equatorial and give cellulose the firm structure.[10] Cellulose is completely insoluble in normal aqueous solutions as the result of hydrogen bonds creating long chains to cause cellulose to form crystalline structures which are shown in Figure 1-1. Cellulose degrades to

produce anhydrocellulose and levoglucosan during pyrolysis at 240-350°C. Other components in pyrolysis oil such as furan derivatives were also from decomposition of cellulose.



**Figure 1- 1** Hydrogen bonds in cellulose chains[8]

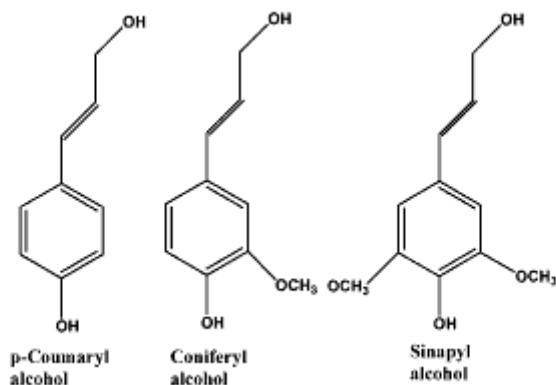
Hemicellulose is the second major constituent that comprises 25-35 wt% of dry wood, 35 wt% of hardwoods and 28 wt% of softwoods.[10] Various units polymerize such as glucose, galactose, xylose, arabinose and glucuronic acid to form hemicellulose. Unlike cellulose, hemicellulose is formed of 100-150 units which is much less than cellulose (5000-10000 units). So, it also has much lower molecular weight. Due to this reason, the temperature range over which decomposition of hemicelluloses takes place during pyrolysis is lower (200-260°C) than cellulose. The main acid content, acetic acid, in pyrolysis oil is formed by deacetylation of hemicellulose. The main components in hemicellulose are shown in Figure 1-2.



**Figure 1- 2** Main components of hemicellulose[8]

The third major constituent is lignin, which accounts for 24-33 wt% of softwoods and 19-28

wt% of hardwoods. It provides mechanical strength for plants because it has a highly branched polyphenolic structure. However, lignin lacks an ordered repeating unit. Instead, it is comprised of various bonded hydroxyl- and methoxy-phenylpropane units.[11] The main three monomeric phenyl-propane units with the p-coumaryl, coniferyl, and sinapyl structures showed in Figure 1-3. At 280-500°C, lignin decomposes while producing phenolic compounds via breaking of ether and carbon to carbon single bonds. Lignin is more difficult to dehydrate than cellulose or hemicellulose and contributes more to char production during pyrolysis processing.



**Figure 1- 3** Main monomeric phenyl-propane units in lignin[8]

### 1.3. Properties of pyrolysis oil

Pyrolysis oil is a solution of cellulose, hemicellulose decomposition products and phenolics decomposed from lignin. Lignin and cellulose can be roughly represented by CH<sub>1.4</sub>O<sub>0.6</sub> with oxygen accounting for 42 wt%. Oxygen present in pyrolysis oil after pyrolysis is in the form of more than 300 compounds. Chemically, most of these compounds are aldehydes, ketones, water, guaiacols, catecols, syringols, vanillins, acetic acid, and formic acids. These compounds give pyrolysis oil high polarity and high hydrophilic nature that make it immiscible with hydrocarbon, like petroleum.[6] The main constituents of pyrolysis oil from various biomass feedstocks are shown in Table 1-2.[8]

**Table 1- 2** Comparison between pyrolysis oil and traditional heavy fuel

<b>Physical property</b>	<b>Pyrolysis oil dry-wet</b>	<b>Heavy fuel oil</b>
Water content, wt %	15-30	0.1
pH	2.5	-
<hr/>		
Elemental , wt %		
<hr/>		
C	54-58	85
H	5.5-7.0	11
O	35-60	1.0
N	0-0.2	0.3
S	0-0.05	2.3
Ash	0.3-0.5	0
Viscosity (50°C), cP	40-100	180
Solids, wt%	0.2-1	1

### 1.3.1. Water content

Water in pyrolysis oils is caused by the moisture left in the feed stock and the dehydration reactions during pyrolysis process. It is up to 15-30 wt % in pyrolysis oil depending on different reaction conditions and feedstock.[5] Some of the water is from the aldehyde hydrates, while the rest is most likely hydrogen bonded to polar organic compounds, which are mostly from the decomposition of carbohydrates.[12] The water content in pyrolysis oil has both negative and positive effects.[13] On one hand, it helps to reduce the viscosity of pyrolysis oil. In addition, water leads to keep temperature uniform in the engine that is important for suppressing NO<sub>x</sub> formation, which makes burning pyrolysis oil to be more environmentally friendly. Moreover, formation of soot is inhibited by O-H radical in water. On the other hand, water in pyrolysis oil lowers the heating value and flame temperature and causes an increase in ignition delay and then reduces the combustion rate. Furthermore, aqueous and heavier organic phase separation will happen if too much water is in pyrolysis oil. Therefore, it is significantly important to minimize the amount of water in pyrolysis oil.

### **1.3.2. Oxygen content**

The oxygen content in pyrolysis oils is usually 35-60 wt %, which mostly can be found in the water in pyrolysis oil. The rest of the oxygen is combined into more than 300 compounds.[6] The distribution of these compounds is basically determined by the processing conditions of pyrolysis such as temperature, residence time and heating rate. As mentioned earlier in this chapter, organic compounds, mainly acids, alcohols, aldehydes, ketones, esters, sugars, phenolic compounds in pyrolysis oil set it apart from hydrocarbons and result in lower energy density. Therefore, oxygen removal from pyrolysis oil and upgrading to transportation fuels is the main goal of this project.

### **1.3.3. Acidity**

The pH value of pyrolysis oil is 2-3 making it very acidic. It is caused by degradation of hemicellulose. This degradation produces acetic acid, formic acid and other carboxylic acids that leads to pyrolysis oil acidity. For this reason, it is reported that raw pyrolysis oil is very corrosive especially for aluminum, nickel based materials and carbon steel.[14] In addition, its corrosiveness increases with the rise of water content or temperature. Simple neutralization would cause rapid polymerization of polyphenols, and so any attempts for such neutralization would be inappropriate; therefore, using other methods to upgrade pyrolysis oil is an acceptable alternative to produce transportation fuels.

### **1.3.4. Viscosity**

The viscosity of pyrolysis oil is on the scale of 35-1000 cP at 40°C depending on its feedstock, process parameters, water content, and storage conditions. Though a high water content leads to reduced viscosity, it also affects the quality of pyrolysis oil itself. Therefore, other polar solvents such as methanol or acetone are considered for mixing with pyrolysis oil to decrease its viscosity. It has been found that the pyrolysis oil viscosity decreases much faster than petroleum with

increase of temperature. Although pyrolysis oil is very viscous, it can be pumped after a appropriate preheating. However, pyrolysis oil ages and tends to become more viscous when stored at high temperatures because the unsaturated carbon compounds in pyrolysis oil are active for polymerization and polycondensation at higher temperature.[13]

### **1.3.5. Solids and ash**

Char particles in pyrolysis oil are formed during pyrolysis. Solid content usually ranges from 0.3-3.0 wt %. It contributes to the catalyst deactivation during catalytic reactions. It also can cause knocking problems in engines if pyrolysis oil is used without upgrading. Furthermore, solids increase the viscosity of pyrolysis oil, leading to difficulties in pumping and atomization. Char particles could act as catalysts to accelerate aging of pyrolysis oil, so removal of solid particles is needed.[15] There are two effective ways. One is called hot vapors filtration, which is analogous to hot gas cleaning in gasification process and removes char particles after the cyclone and before liquid collection. This process is very effective but comes at an expense of lower oil yield due to increased residence time and catalytic cracking on the char layer on the filter.[16] Another method is called liquid filtration, which is a traditional way. In contrast of hot vapor filtration, it is a cheaper way but far less effective.

Ash in pyrolysis oil is mostly alkali metals such as potassium, sodium, calcium and vanadium. Calcium is responsible for hard deposit. The presence of ash content above 0.01 wt% is highly undesirable because it can cause erosion, corrosion and even deterioration in engine; however, since the ash particles are very fine and so are able to slip through the filters, it is very difficult to remove ash from pyrolysis oil by filtration.[16, 17]

### 1.3.6. Combustion behavior

Combustion properties play an important role in the application of pyrolysis oils in standard engines. Pyrolysis oil is combustible but not flammable (due to high percentage of non-volatile components).[18] Pyrolysis oil needs high energy to ignite but it can sustain the flame if it ignites.[13] There are two ways to test combustion properties of pyrolysis oil. The test can be performed by employing a fiber-suspended single droplet or a stream of free-falling droplets. The single droplet method gives one the ability for simultaneous measuring of the droplet temperature when recording the changes. High pressure combustion behavior of liquid fuels can be studied using this method. The biggest disadvantage is the droplet size is determined by the fiber size. Meanwhile, the advantages and disadvantages of free-falling droplet method are opposite to the single droplet method.[15]

An extensive study on combustion properties of pyrolysis oil was performed at Sandia National Laboratory.[19] The experiment was performed using the single droplet method which displayed several states of combustion comprised of: ignition, quiescent burning, micro-explosion, destructive sooty burning of droplet fragments, generation and burnout of cenosphere particles. Meanwhile, combustion of petroleum droplet under the same conditions displayed only quiescent and sooty burning form ignition through burnout.

The unique feature of micro-explosion in pyrolysis oil has significant impacts on the heat releasing rate, droplet burning time and extent of cenosphere formation. Nonetheless, the burn times of pyrolysis oil are comparable to No. 2 fuel oil under similar conditions. It was found that droplets with less severely cracked pyrolysis oil exhibited a less effective micro-explosion and longer burnout times compared with No. 2 fuel oil (180 ms vs 110 ms). Meanwhile, severely cracked pyrolysis oil droplets showed more violent micro-explosion resulting in shorter burnout



time.[15] Ignition of pyrolysis oil is difficult partly due to the high water content. Currently pyrolysis oil can be ignited using a pilot flame or preheating of combustion chambers. This can potentially be a disadvantage over petroleum fuels.

#### 1.4. Pyrolysis oil upgrading methods

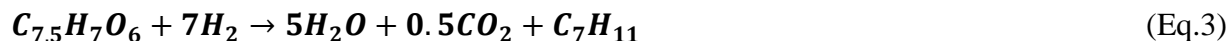
Pyrolysis oil is an acidic, unstable, and viscous liquid with solid particles and large amount of water that makes it necessary to upgrade to use it as a transportation fuel. There are five main methods: 1) Catalytic hydrotreating, 2) Fluid catalytic cracking, 3) High pressure thermal treatment, 4) Emulsification, and 5) Esterification.

##### 1.4.1. Catalytic hydrotreating

Pyrolysis oil can be stabilized and converted into a hydrocarbon fuel by removing oxygen as water and CO<sub>2</sub> via catalytic hydrotreating. The method of catalytic hydrotreating has been used to remove nitrogen and sulfur in the petroleum industry, but economical removal of oxygen in pyrolysis oil is still in the research stage. The upgrading step involves contacting the pyrolysis oil with high pressure hydrogen (3000 psig) and at moderate temperatures (<400°C) in various reactors. A dual-stage hydrotreating is the preferred method for pyrolysis oil because single stage hydrotreating has proved to be difficult as excessive coke formation that results in catalysts deactivation.[6] In a dual-stage hydrotreatment, initially mild hydrotreating is required to stabilize pyrolysis oil and then followed by more severe hydrotreating conditions for oxygen removal. The oxygen in pyrolysis oil is removed by a combination of hydrodeoxygenation (HDO) (Eq. 1) and decarboxylation (Eq. 2)



Catalytic hydrotreating of pyrolysis oil can reduced oxygen content to less than 2%. The treatment of pyrolysis oil concurrently produces water and off-gas. The water phase contains water soluble organics, while the produced gas contains carbon monoxide, carbon dioxide and light hydrocarbons (methane, ethylene propylene, etc.). Typically, the yield of upgraded pyrolysis oil is about 45% (Eq.3).



Catalytic hydrotreating has some disadvantages such as requiring higher temperature and hydrogen pressure to ensure hydrodeoxygenation level, and because of polymerization, coke is formed, which would deactivate catalysts, but the results are very desirable and economically feasible. Cost analysis by Jones[6] in 2007 showed, the average refinery prices for gasoline and diesel were \$2.18/gal and \$2.20/gal respectively. The estimated production price for upgraded pyrolysis oil would be \$2.04/gal. This makes pyrolysis oil economically more attractive than gasoline and diesel.

#### **1.4.1.1. Catalysts and reaction mechanisms**

##### **1.4.1.1.1. Sulphided catalysts**

In early work, catalysts chosen for hydrotreating were those for petroleum processing technology, such as sulphided catalysts. Sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> are two common active catalysts for hydrodeoxygenation at 200-350°C. Senol[20] found the activity of catalysts had been greatly increased by sulphidation. They conducted several experiments at 255°C- 300°C on sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub> with 1.5MPa (215psi) H<sub>2</sub> running for 4 hours. The result showed that the main products were alkenes but the conversion rates were low at 45.9% and 27.1% respectively. Though NiMo sulfide is more active than CoMo sulfide for selective hydrocarbon formation, the sulphided CoMo worked in better temperature range. The product distribution consisted mostly of n-heptane and n-hexane. The alcohols were found in very small amounts.

In another study[21], the deoxygenation reaction in light gas oil over sulphided NiMo/Al<sub>2</sub>O<sub>3</sub> at 45 bars of H<sub>2</sub> and 350°C was studied. The yield of deoxygenated products from rapeseed oil was up to 64% but there was still significant aromatic product left in upgraded pyrolysis oil.

The activity of sulphided catalysts depends on the concentration of sulfide. Catalysts are more active with relatively low sulfide concentration (500 ppm) than with high sulfide loadings (20000 ppm)[22]. In petroleum refining industry, sulphided catalyst is well known for hydrodesulfurization since heavy petroleum fuel contains high sulfur (2-3%) which is ten times more than in pyrolysis oil (<0.2%). Another reason to choose sulphided catalysts in petroleum refining is that the high content of sulfur(S) may poison the non-sulphided catalysts resulting in deactivation. In our study, sulfur would be converted to H<sub>2</sub>S, which is not environmental friendly and it has to be removed from hydrogenated products. So it means the conventional HDS catalysts are not suitable for pyrolysis oil hydrotreating process. Therefore, using non-sulphided catalysts could avoid this desulfurization step. In addition, the conventional hydrotreating catalyst is less suitable for pyrolysis oil upgrading due to sulphur causing product contamination and poor stability in the presence of water in pyrolysis oil. Thus, the development of non-sulphided catalysts for pyrolysis oil upgrading is necessary and environmentally favorable. That is why recently non-sulphided catalysts have been introduced into pyrolysis oil upgrading processing and have received more attention.

#### **1.4.1.1.2. Noble catalysts**

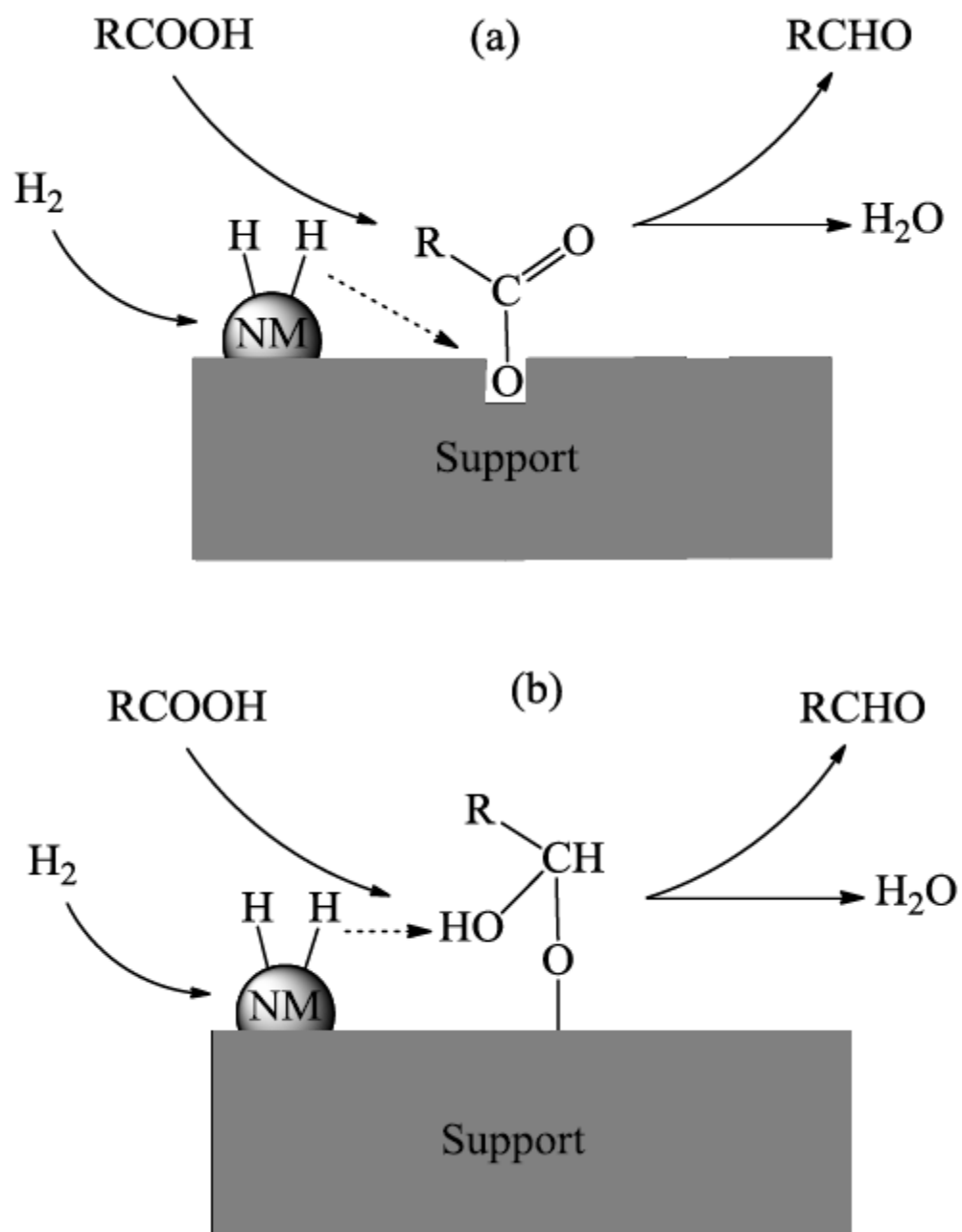
The development of non-sulphided catalysts for hydrodeoxygenation reaction in pyrolysis oil upgrading processing is based on two factors. First, it must be a transition metal, which is in its reduced state that requires activating with dihydrogen. Second, this transition metal should be an oxide form with variable valence that is activated with oxy-groups in the oxygen compounds. Thus metals such as Co, Mn, Mo, S and Zr are suitable for the activation of oxygen compounds. The

noble metals like Platinum (Pt) and Palladium (Pd) have been widely used for hydrotreating since hydrogen is easily activated and split on interface or surface to react with other components in pyrolysis oil. The mechanism is that H<sub>2</sub> is adsorbed and activated on the noble metal sites and oxygenated compounds are adsorbed and activated on noble metal sites or the support interface. The adsorbed H atoms on noble metal sites react with O atoms on oxygenates resulting in the cleavage of C-O bond and produce H<sub>2</sub>O. The HDO mechanisms over noble metal is shown in Figure 1-4 a. Jelle Wildschut[5] has tested Ru/C, Rh/C, Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Pt/C, and Pd/C at 250°C or 350°C with 200 bar (2880 psi) for 4 hours. The oxygenation level as function of upgraded oil yield is shown in figure 1-5. The Rh/C is a potential catalyst to attain high yields (up to 65%) of upgraded pyrolysis oil but the higher amount of oxygen compounds in the product and higher hydrogen consumption must be taken into account. Ru/C appears to be the most promising catalyst for hydrotreating. The O/C value over Ru/C after HDO is 0.1 and H/C is 1.4, indicating that the products are partially deoxygenated. The ratios of O/C and H/C are related to higher heating value (HHV) of upgraded products. The calculation of HHV by elemental composition is shown in equation 4.[23] The best operating temperature for non-sulphided catalysts is below 400°C because coke formation would cause deactivation of catalysts.[5]

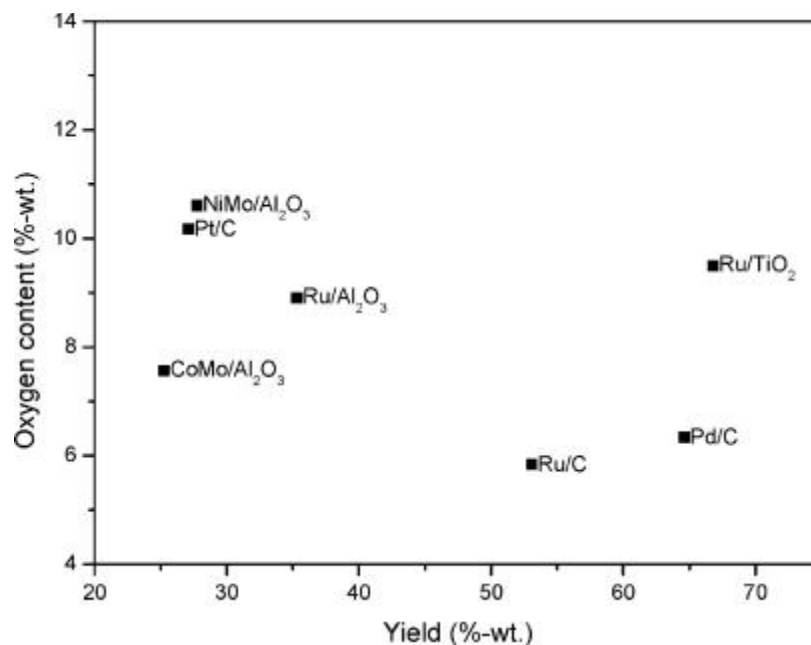
$$HHV \left( \frac{MJ}{kg} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211ash$$

(Eq.4)

For oxide noble catalysts, Mars and Van Krevelen mechanism is involved.[24] The mechanism is shown in figure 1-4 b. It can be explained as follows. The lattice oxygen reacts with H<sub>2</sub> creating oxygen vacancies followed by refilling with oxygen from oxygenated compounds. Oxygen is thus cleaved from C-O to generate final deoxygenated products.



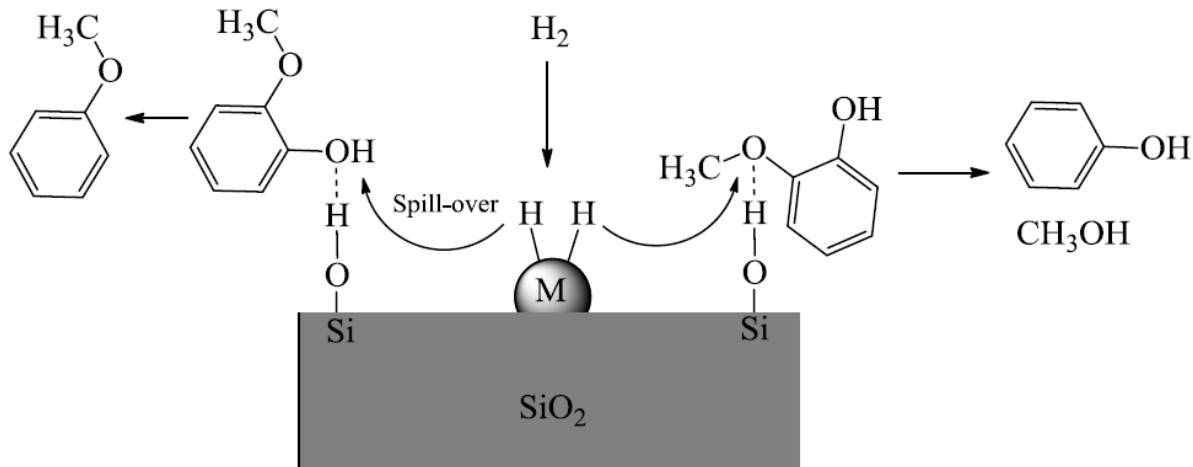
**Figure 1- 4** HDO mechanism of acids over noble metal (NM) supported catalysts. (a) Noble metal (b) Oxide noble catalysts[25]



**Figure 1- 5** Effects of Different non-sulphided catalysts on deoxygenation (graph taken from Refs 2). The x axis is the yield of liquid pyrolysis oil after upgrading and the y axis is remaining oxygen (wt %) in pyrolysis oil after HDO

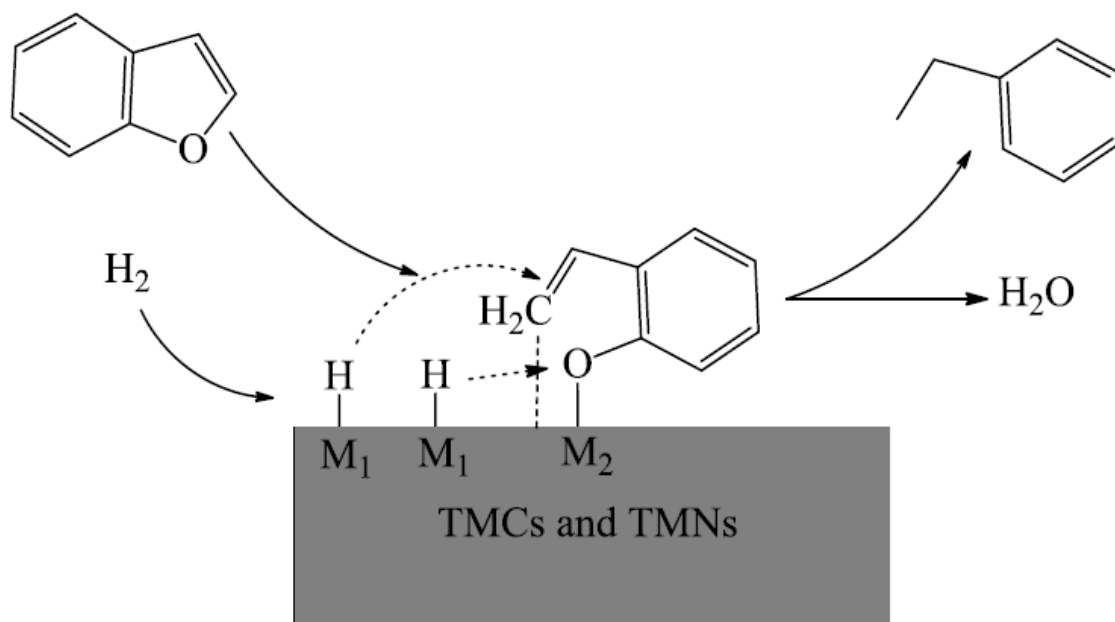
#### 1.4.1.1.3. Non-precious metal catalysts

Although supported noble metal catalysts are very active in HDO of pyrolysis oil process, one of the main challenges for its application is the cost. Non-precious metal catalysts such as Ni/Al<sub>2</sub>O<sub>3</sub> and Fe/SiO<sub>2</sub> were studied and found to be very active. In Dufour's study, Fe/SiO<sub>2</sub> was used for HDO of model compound, guaiacol, at 350-450°C.[26]. Guaiacol is activated by acidic OH sites from SiO<sub>2</sub> and reacts with absorbed H<sub>2</sub> on the surface of Fe causing C-O cleavage. The mechanism of guaiacol HDO over Fe/SiO<sub>2</sub> proposed is shown in figure 1-6. HDO over Ni based catalysts at 300°C and 1MPa was reported by Yakovlev and HDO degree of 95% was obtained. Bimetallic Ni-Cu supported catalysts are even more active for HDO than Ni. The highest HDO degree of 99% was gained using Ni-Cu/Al<sub>2</sub>O<sub>3</sub>. [27] The reason is that Cu is found to facilitate hydrogen spillover, thus helping nickel oxide reduction and then forming substitution solid solution with Al<sub>2</sub>O<sub>3</sub> support.



**Figure 1- 6** Proposed mechanism of HDO of guaiacol over Fe/SiO<sub>2</sub>. (based on Refs 19)

Transition-metal carbides (TMCs) such as Mo<sub>2</sub>C, NbC, NiMo carbide are normally produced by temperature programmed reduction (TPR) or carbothermal hydrogen reduction.[28] Transition-metal nitrides (TMNs) such as Mo<sub>2</sub>N, VN and WN are prepared by TPR with ammonia.[29] TMCs and TMNs also show good activity in HDO as noble metal catalysts, and moreover, they are resistant to S, N and O.[28] The carbon atoms in TMCs permeate into the transition metals that induce increased distance of metal-metal and thus enlarge the d-band electron density at Fermi level of transition metals.[30] In regards to TMNs catalysts, the unsaturated metal sites and oxynitride species from support surface or on the subsurface of nitride are related to the HDO activity. Oyama studied benzofuran HDO over various TMCs and TMNs catalysts at 370 °C and 450 psi. Ethylphenol and ethylcyclohexane were produced as main products. Among the various catalysts, VN showed the best activity because of the optimal binding energy for hydrodeoxygenation of pyrolysis oil.[31]. The reaction mechanism over TMNs or TMCs is shown in figure 1-7.



**Figure 1- 7** Proposed mechanism of HDO of benzofuran over TMNs and TMCs catalysts (M1: unsaturated metals, M2: C or N) (Drawn based on Refs 24)

#### 1.4.1.2.Supported catalysts

Active catalysts play an important role for HDO of pyrolysis oil process. However, supported catalysts are also very crucial by decreasing the cost of catalysts, and stabilizing active phases.[32] In addition to that, supported catalysts provide active sites such as acid sites which interact with active catalysts leading to new active phases forming on the surface.[32]

Mesoporous materials such as silica have large apertures and pores that improve the molecular diffusion rate , especially for large organic molecules.[33] Comparing with  $\gamma$ - $\text{Al}_2\text{O}_3$ , mesoporous materials have more active acid sites and much higher surface area.[34]

Silica itself is an inert support catalyst. According to reports,  $\text{SiO}_2$ -based catalysts show better selectivity and more activity than  $\text{Al}_2\text{O}_3$ -based catalysts because support acidity and metal- support interactions play main role on its activity.



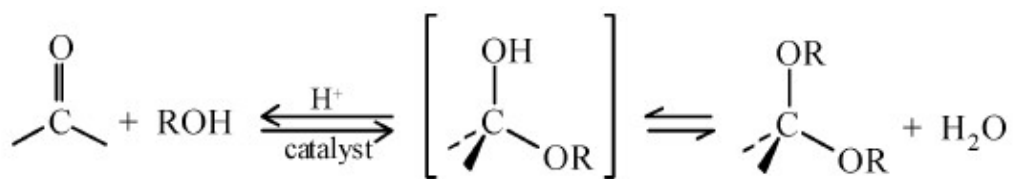
Activated carbon (AC) has been suggested to be a more promising support than alumina or silica because of low cost and low coking tendency. The very high surface area of AC allows for a high dispersion of activated catalysts. However, the increasing active metals loading favors sintering because of the weak interaction between AC and active catalysts leading to micropore blocking. Also, part of active metals deposit in micropores is wasted in HDO reaction involving large molecule compounds from pyrolysis oil.[35]

#### **1.4.1.3.Solvent effect**

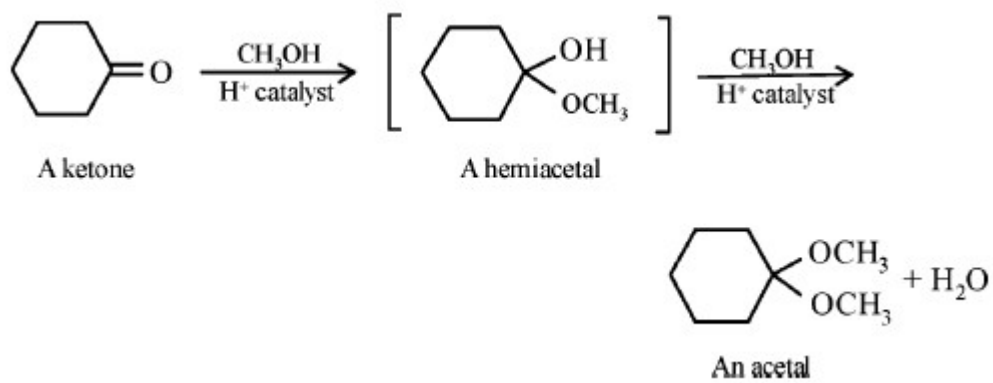
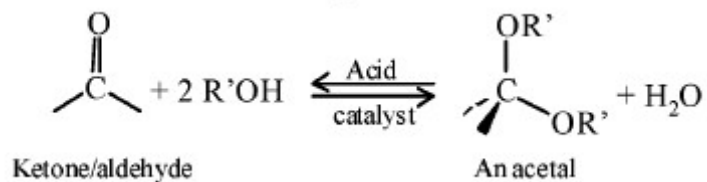
As pyrolysis oil ages and become more viscous during storage, adding solvent to decrease its viscosity has drawn attention in the pyrolysis oil research.[36] Polar solvents are used to homogenize pyrolysis oil. The addition of polar solvents also enhances the solubility of water-insoluble compounds, like high molecular weight mass lignin [24] in pyrolysis oil. Among polar solvents, water, methanol, and furfural have been reported as having better effects on pyrolysis oil.[16, 37] Methanol shows a significant effect on pyrolysis oil stabilization. By adding 10 wt % methanol, the viscosity of pyrolysis oil decreases almost 20 times less than without additive.[16] Below are three major mechanisms impacted by adding solvents for decreasing the viscosity of pyrolysis oil.

- (1) Physical dilution pyrolysis oils without affecting the chemical reaction rate.
- (2) Reducing the reaction rate by molecular dilution or changing the microstructure of liquid.
- (3) Chemical reactions between the pyrolysis oil and solvent that avoid further chain growth.

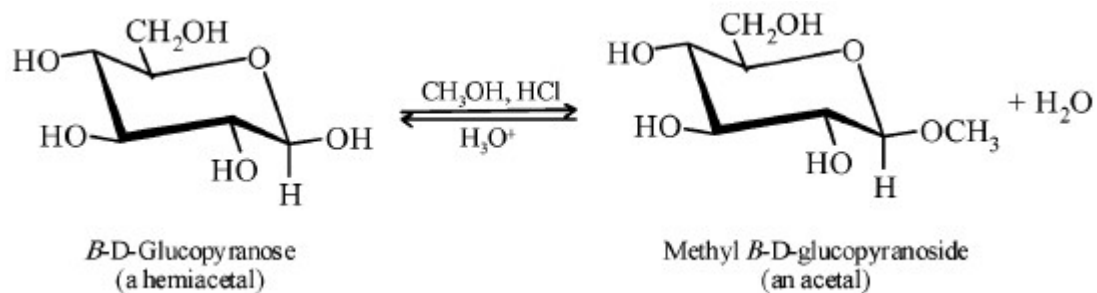
The reaction between alcohol and pyrolysis oil is called esterification (Figure 1-8) and acetalization (Figures 1-9 and 1-10). Considering the cost, alcohols are the most promising solvent for upgrading the quality of pyrolysis oil.



**Figure 1- 8** Esterification of aldehydes and ketones[38]



**Figure 1- 9** Hemiacetal and acetal formation from aldehydes and ketones[38]



**Figure 1- 10** Acetal formation from monosaccharides[38]

Another category of solvents consists of alkanes (hexane, decane, Hexadecane, etc.).[31] They are insoluble with pyrolysis oil because they are non-polar solvents, however, they have very good solubility for hydrogen at certain conditions, and when combined with a suitable catalyst, it is able to act as effective hydrogen donor solvent called “hydrogen shuttling” mechanism. Furthermore some non-polar compounds in pyrolysis oil could dissolve into alkanes and then keep the alcohol in the oil phase that promotes products separation.

#### 1.4.2. Fluid catalytic cracking (FCC)

Fluid Catalytic Cracking (FCC) can convert oxygenated compounds to lighter hydrocarbon fractions in the range of gasoline boiling. To compare with the process of catalytic hydrotreating, FCC does not need hydrogen and can be done at atmospheric pressure.[39] It is also considered a cheaper alternative to hydrotreatment.[40] The first commercial catalyst, HZSM-5, which was invented by Mobil for the methanol to gasoline (MTG) process, was widely used for FCC study.[41] However, due to the high yield of coke formation (10-25 wt %) and low quality of products (phenol derivatives ~20 wt %), the resolution of these issues is still ongoing for the application of FCC. Other conventional cracking catalysts have been evaluated and some of them increase the productivity of non-aromatic hydrocarbons but the coke formation problem becomes worse. A less severe temperature (below 400°C) was successful in reducing the yield of coke to 4- 15 wt% but the oxygenated compounds increased in liquid products.[40] So, FCC has been proved not to be a good choice for pyrolysis oil upgrading over commercial catalysts and conditions so far. The yield of upgraded pyrolysis oil is 26% as shown below in Eq.5.



### **1.4.3. High pressure thermal treatment**

In contrast to catalytic cracking and HDO, high pressure thermal treatment does not employ any catalyst. Also, despite HDO, hydrogen is not used for upgrading and pressurizing is achieved with nitrogen. This appears to be an advantage over HDO which may improve the economics of upgrading. Recently, an interesting study on upgrading fast pyrolysis oil via high pressure thermal treatment was published.[42] In this study, a tubular reactor was designed to determine the effect of temperature and residence time on quality and yield of produced oils from fast pyrolysis oil at 200 bar (2900 psi). A high pressure is needed to keep water in liquid state, as evaporation of water leads to extensive char formation. The temperatures between 200 and 350 °C and a residence time between 1.5 - 3.5 min were examined. The oil fraction molar mass increase and sugar content in aqueous fractions decrease were observed at the same time by increasing the temperature. However, the residence time did not have as strong an effect as temperature indicating that polymerization reactions were very fast. It might be concluded that polymerization of sugars was one reason that accounted for pyrolysis oil molar mass increase. The molar mass increase of produced oils via high pressure thermal treatment is the major drawback of this upgrading route.

### **1.4.4. Emulsification**

Due to the unstable nature of pyrolysis oil, it is difficult to use in neat form as a fuel. Emulsification of pyrolysis oil with diesel is the simplest way to use pyrolysis oil as a transportation fuel. Ikura[43] conducted experiments where pyrolysis oil was emulsified in diesel fuel. Prior to emulsification, the pyrolysis oil was centrifuged to remove heavy fractions of pyrolysis oil. A series of emulsification runs determined the process conditions, processing costs and emulsion stability. A stable emulsion formation required surfactant concentration ranging from 0.8 wt% - 1.5 wt% based on power output and pyrolysis oil concentration. In his work, he

claimed A newly CANMET surfactant was estimated to cost 2.6 cents/L for 10% emulsion, 3.4 cents/L for 20% and 4.1 cents/L for 30%. The viscosities of the 10-20% emulsion pyrolysis oil were significantly lower than the untreated pyrolysis oil. The corrosiveness of the mixture was half of the pyrolysis oil alone.

#### **1.4.5. Esterification**

Hilten[44] developed a reactive condensation technique to decrease the concentration of reactive compounds in pyrolysis oil thus increasing the overall quality of pyrolysis oil. Pyrolysis oil was esterified with ethanol at elevated temperature of 114-127°C and reactor residence time of 60s. GC (Gas Chromatography) analysis indicated formation of esters; decrease in acetic acid by nearly 42% resulted in increase of pH from 2.5 to 3.1; reduction in viscosity from 24.4 to 9.7 cSt at 40°C; decrease in water content from 10 wt% to 8 wt%. Esterification is an effective way to treat acids under milder conditions. Except for unsaturated compounds and lignin-derived oligomers, which do not involve esterification reaction. In addition, the highest pH value after esterification is still too high thus, pyrolysis oil upgrading to transportation fuel via this method is not feasible.

With this background, it is apparent that more economical methods are needed to upgrade pyrolysis oils. This thesis is focused on this aspect.

## Chapter 2: Materials and Methods for Batch Mode Runs

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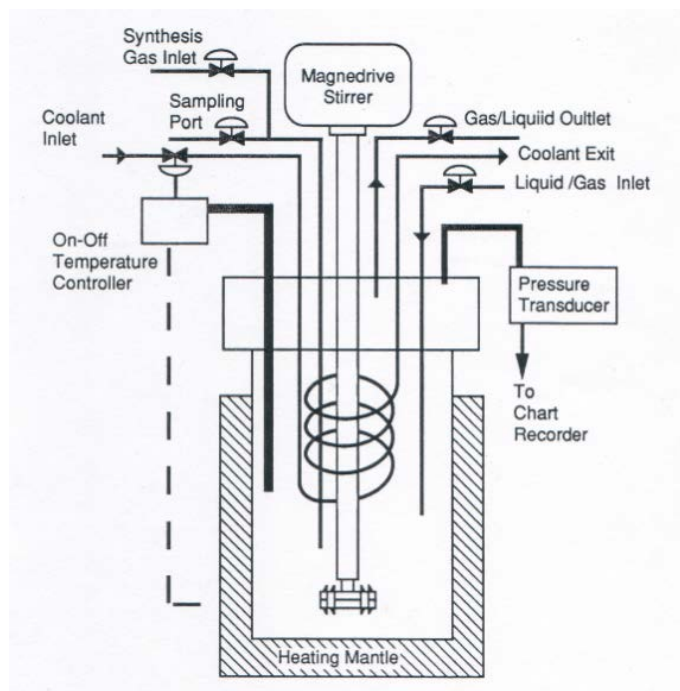
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## 2.1. Materials

Three samples of pyrolysis oil, derived from corn stover, soybean straw and switchgrass were provided by the United States Department of Agriculture (USDA)-Agricultural Research Services (ARD) in Wyndmoor, PA. The switchgrass pyrolysis oil was produced from fast pyrolysis of switchgrass at a feeding rate of 2.5 kg/h in a fluidized bed reactor under a nitrogen atmosphere at 500°C. Transition metal catalysts, 5 wt% Ru on C, 5 wt% Rh on C, 5 wt% Ru on Al<sub>2</sub>O<sub>3</sub>, 5 wt% Rh on Al<sub>2</sub>O<sub>3</sub>, NiCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CoCl<sub>2</sub>, Ru (bipy) (CO)<sub>2</sub>Cl<sub>2</sub> were supplied by Sigma-Aldrich. The solvents, polyethylene glycol (PEG) solvent (>99 %, mol. Wt. 380-420), hexadecane (anhydrous, >99 %) were also obtained from Sigma-Aldrich. Hydrogen (HP grade), Helium (UHP grade) and Compressed Air (Dry grade) were obtained from Praxair.

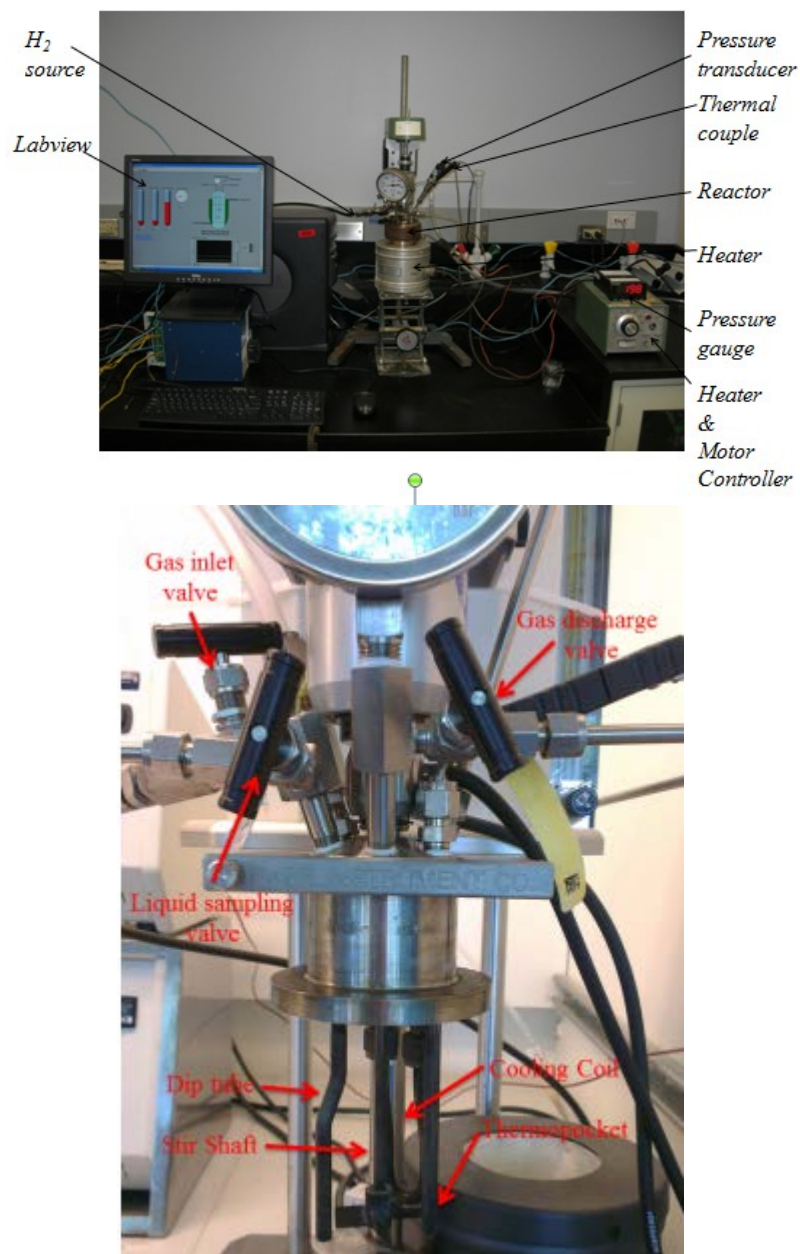
## 2.2. Apparatus

A 300 Parr batch unit was used for catalytic pyrolysis oil upgrading experiments (Figure 2-1). A picture of the setup is given in Figure 2-2.



**Figure 2- 1** A 300 mL Parr batch unit for catalytic pyrolysis oil upgrading





**Figure 2- 2** Batch unit set up for pyrolysis oil upgrading

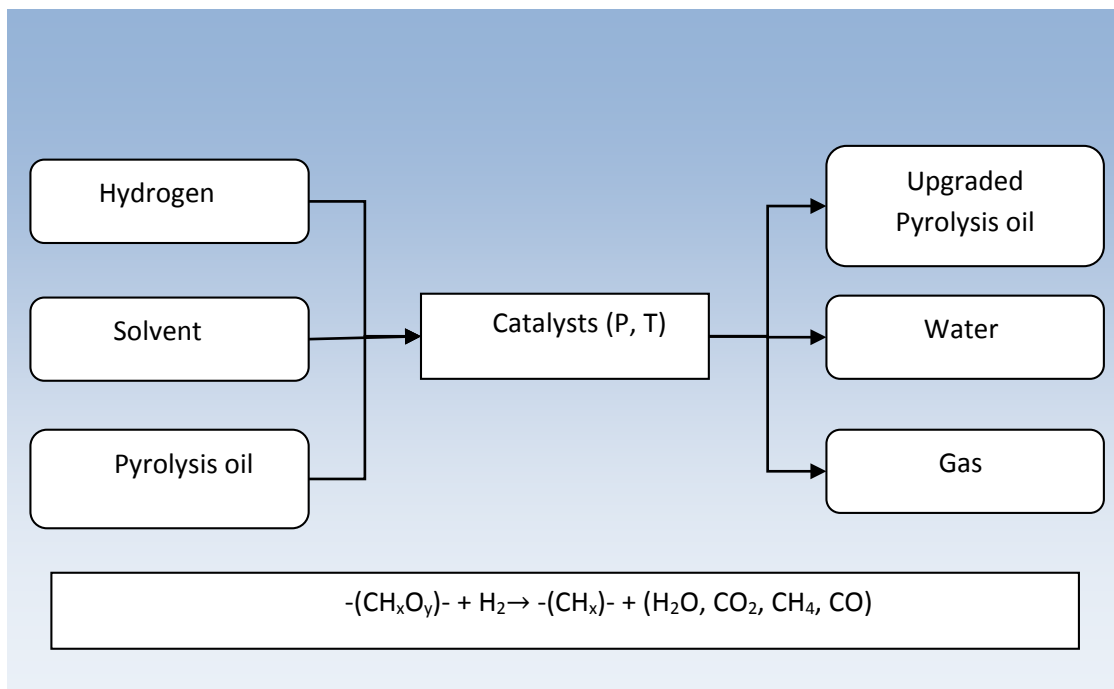
Batch experiments were performed in a 4566 mini bench top reactor unit from Parr Instrument Company. The top of the reactor is attached to the support stand of the setup, which ensures that all attachments are permanently in place. The reactor container is a 300ml hollow cylinder. A cover clamp with a total of 6 bolts is used to attach and tighten this to the top. A polytetrafluoroethylene (PTFE) gasket is placed between the reactor container and the top. This ensures tight sealing of

the reactor during operation at high pressure. The maximum operating pressure is 3000 psig. The minimum volume in the container was 70-80 ml to ensure proper mixing by the stirrer and maximum volume by Parr advised as 2/3 of the maximum volume. The magnetic driven stirrer can be adjusted to a speed between 0-700 rpm. Adjustment knob is on the controller. A J type thermocouple inserted on the top part will give accurate measurement of the actual temperature in the reaction solution. Three valves are connected to the fixed top: gas inlet valve, liquid sampling valve and gas release valve. They are all accurate needle valves. When closing them, over tightening must be avoided.

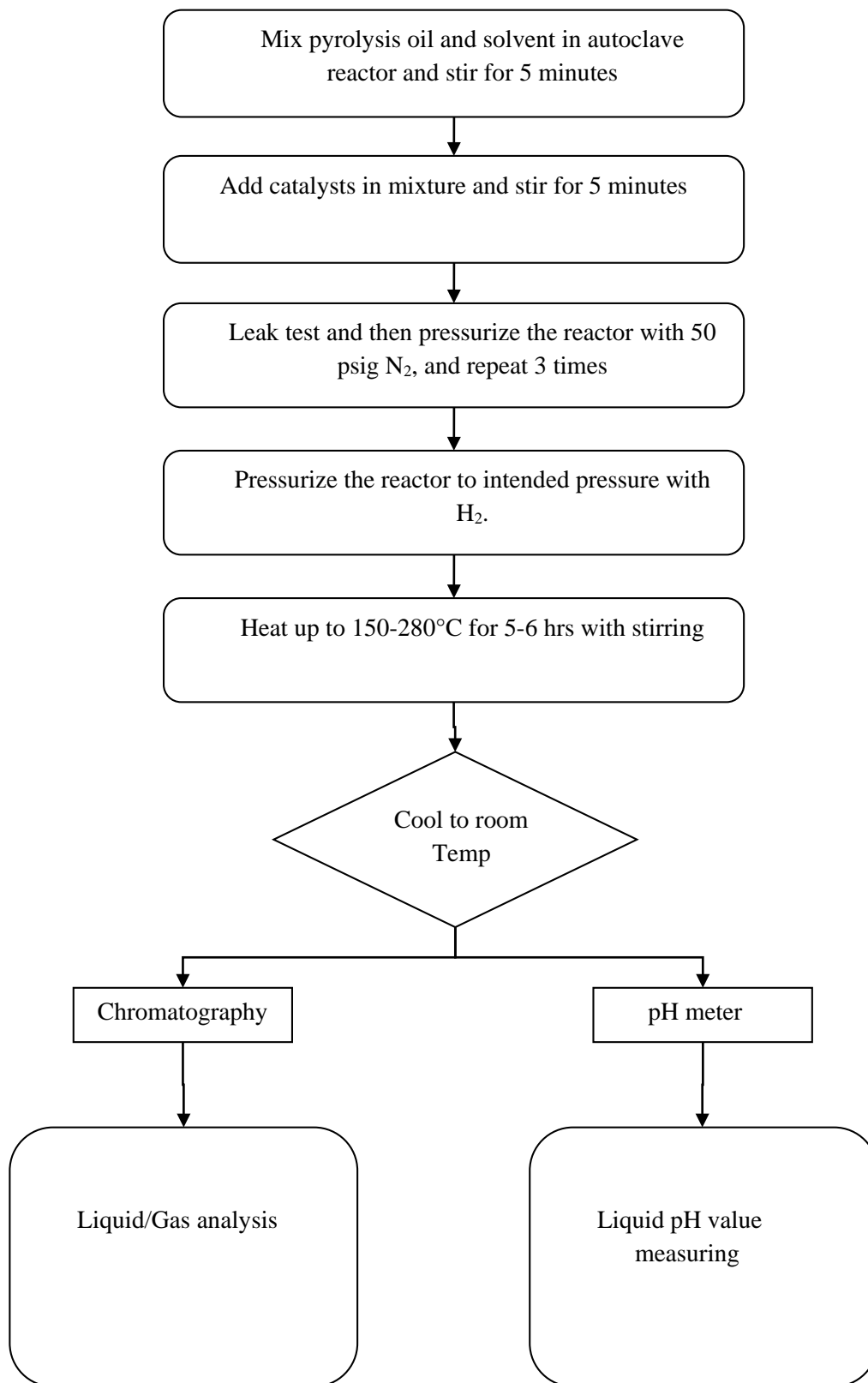
### **2.3. Hydrogenation experiments**

In a typical experiment, 10 ml pyrolysis oil was mixed with 90 ml solvent in a 100ml graduated cylinder and then put into the 300 ml autoclave reactor equipped with a magnetically driven stirrer. PEG, hexadecane and distilled water were used as solvents. After stirring the mixture of pyrolysis oil and PEG, the two liquid phases became a uniform solution. This process greatly decreased the viscosity of pyrolysis oil. Hexadecane is a nonpolar solvent and it is immiscible with pyrolysis oil. However hydrocarbons that are produced during the reaction went into hexadecane which made products analysis easier. After addition of 0.1-0.6g catalyst, the reactor was sealed and then purged with 50 psi nitrogen for 3 minutes to remove air and then pressurized with H<sub>2</sub> to the intended pressure (150-1000 psig). The reactor was heated to the desired temperature (150-280°C) and the temperature was maintained for 5-6 hours. The reactor temperature and pressure were monitored and recorded by a LABVIEW-based data acquisition unit. After the completion of the experiment, the reactor was cooled down to ambient temperature. A 0.5 ml gas sample was syringed from the gas port of the reactor for analysis. After recovering liquid samples, acetone was used to rinse the reactor and then filtered by vacuum filtration method with No. 50 filter paper.

Subsequently, the filter paper was dried in the oven at 80°C and then weighted. The weight of solid minus the weight of original catalyst used was the solid formed during HDO reaction and the remaining liquid product was stored in a refrigerator for further analyses. Experiments were repeated to establish the reproducibility of the runs. Experimental processes are shown below in Figure 2-3. The experiment flow chart is shown in Figure 2-4.



**Figure 2- 3** Simple experimental processes



**Figure 2- 4** Experiment flow chart

## **2.4.Product gas analysis**

Gas Chromatography (GC) is used to separate components of a mixture. A small amount of the sample to be analyzed is drawn up into a syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the sample is injected. A carrier gas, such as nitrogen or helium, flows through the injector and pushes the gaseous components of the sample onto the GC column and are separated by column. Multiple gas chromatographs (GCs) were used to precisely analyze gaseous products from runs. Two Gow Mac Series 580 gas chromatographs (GCs) equipped with TCD (thermal conductivity detector) detectors were used to analyze CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>. All other light hydrocarbons gases in the products were analyzed by a PerkinElmer Clarus 580 equipped with a TCD detector.

### **2.4.1. Characterization of carbon dioxide and methane**

One Gow Mac Series 580 GC was equipped with two packed columns: 1/8" carboxen 1000 for the analysis of CO<sub>2</sub> and CH<sub>4</sub>, and 1/8" molecular sieve 5Å (80/100 mesh) for the analysis of CO. Both columns required helium as a carrier gas at a flow rate of 25 ml/min. Tank delivery pressure was set at 40 psig. The specifications of GC analysis of CO<sub>2</sub> were: injector temperature: 90°C, detector temperature: 150°C and oven temperature: 80°C. The GC set up for CO were: injector temperature: 80°C, detector temperature: 150°C and oven temperature: 80°C. Both GC methods were isothermal. The standard operating procedure (SOP) of using Gow Mac Series 580 GC described as follows.

- 1) Check the carrier gas flow and make sure it is flowing before turning on the GC.
- 2) Set injector, detector and oven temperature to proper value and wait till temperatures are stabilized. Use needle valve to adjust gas flow rate to the desired numbers.

- 3) Open the software, Clarity, and select the right method. Wash a syringe with standard gas by filling the syringe completely and ejecting the standard gas. Repeat this procedure 3-4 times to remove air or any other impure gas residuals from the syringe.
- 4) Standard gas, which is a known composition sample, is used as external standard. Pull 0.5ml of standard gas into the syringe. Before injecting sample into injector, set the detector current of GC to 100-150 mA.
- 5) Repeat step 2 to rinse syringe with gas products and then inject gas products into the GC.
- 6) The area number of gas peaks were compared with the base standard data and the percentage of gases in the reactor were calculated.
- 7) To turn off the Gow Mac GC, bring all the set temperatures to room temperature and set the detector current to minimum value. Turn the GC off and wait for at least 30mins to let the detector to cool down. During this procedure the carrier gas must be still on (very important).
- 8) Close the valve on carrier gas tank.

#### **2.4.2. Characterization of hydrogen**

For hydrogen analysis, another TCD Gow Mac Series 580 GC equipped with 1/4" molecular sieve 5Å (80/100 mesh) was used. The specifications of GC analysis of Hydrogen were: injector temperature: 60°C, detector temperature: 80°C and oven temperature: 60°C. Carrier gas: N<sub>2</sub> at a flow rate of 20ml/min. The test procedures were same as stated in chapter 2.4.1. The key data for H<sub>2</sub> consumption was calculated from the difference between initial and final % H<sub>2</sub> values as measured by GC.

### **2.4.3. Characterization of light hydrocarbons in gas products**

Light hydrocarbons in the products were analyzed by an online PerkinElmer Clarus 580 GC equipped with a TCD detector and four columns. The four columns were: 1) Hayesep N, 2) Molecular Sieve 13X, 3) Molecular Sieve 5Å, 4) Hayesep T. The GC method parameters were: detector T: 200°C; Oven T: 60°C held for 11 min. The carrier gas was helium at 40 ml/min. Gas standards for ethylene, ethane, propylene and propane were used for the calibration of the GCs.

## **2.5.Characterization of liquid samples**

### **2.5.1. GC/MS analysis**

GC-MS analysis of raw pyrolysis oil and treated samples were performed on a Perkin Elmer Clarus 680 GC equipped with a Perkin Elmer Clarus SQ8T mass detector (MS). The GC-MS was coupled to a CDS Pyroprobe 5000 series filament pyrolyzer with trap-mode. For raw pyrolysis oil, 0.24 g (6 wt %) of oil sample was diluted with 3.76 g (94 wt %) of acetone to make it less viscous and suitable for the GC injection. For treated oil samples, dilution was not necessary as they were already mixed with solvent. One microliter liquid sample was syringed into a quartz tube (2.5 cm X 3.0 mm i.d.) and pyrolyzed at 280°C for 2 minutes. The GC column used was Perkin Elmer Elite-5MS (30m x 0.25mm x 1.0 µm). The GC temperature profile was: Injector T: 250°C; Oven T: 45°C/4 min; ramp rate: 3° C/min; Final T: 280°C held for 20 min. Helium was used as carrier gas at a flow rate of 1 ml/min. The split ratio was set to 30:1.

The MS scan range was 33 to 600 m/z at a rate of 0.1 s per scan with interscan delay of 0.1s. The mass spectrometer was calibrated using heptacosafuorotributylamine and tuned prior to analysis. Both interface and source temperatures of MS were 250°C. The m/z values of the fragments of compounds were recorded. The identification of fragments was achieved by matching

m/z values with those in the NIST MS Library Search 2.0. The standard operation procedure of GC/MS is described in the following steps.

- 1) Power up mass spectrograph and wait for front panel light to change from blinking red to blinking green and then start MS software.
- 2) On tune page, click on Options/Pump On to start vacuum. See continued increase in turbo speed up to 100%. Wait for vacuum gauge to get down to green ( $8 \times 10^{-5}$ ). Wait for 3-4 hours before vacuum pump evacuates all air and impurities.
- 3) Take control of GC and start loading methods onto GC and MS. Wait until all the check lights turn to green.
- 4) Wash syringe with acetone 2-3 times and pull some of sample into the syringe. Remove air bubbles in the syringe by rapidly moving the plunger up and down while the needle is in the sample. Usually  $1 \mu\text{L}$  of sample is injected into the quartz tube.
- 5) Click start on Pyroprobe and open chromatograph in TurboMass software to view results.
- 6) After GC/MS test, GC oven temperature will automatically get to room temperature based on method. MS must load "Cool" method to cool down source temperature of MS to  $50^\circ\text{C}$ . Turn off the split gas flow to save carrier gas.
- 7) If GC/MS needs to shut off, click on Options/Pump Off to stop vacuum pump. Observe the vacuum gauge to red zone and wait for the front panel light to change to blinking green and then turn off the GC and the MS.

### **2.5.2. GC analysis**

In order to get quantitative data of liquid sample, PerkinElmer Series 580 GC equipped with FID (flame ionization detector) detector was used. The concept of FID operation is based on the detection of ions produced during combustion of organic samples in a hydrogen flame. The



generation of ions is proportional to the concentration of samples. FID detector is the most sensitive GC detector for any carbon containing liquid organic samples. In our research, Elite-WAX capillary column coated with crossbond-PEG was used to separate oxygenated chemicals. Elite-1 capillary column coated with crossbond 100% dimethyl polysiloxane was used for non-polar chemicals separation such as hydrocarbons. Although PerkinElmer Series 580 GC has an autosampler, calibration curve needs to be finished before sample tests.

### **2.5.3. FI-TR analysis**

FT-IR stands for Fourier Transform Infrared spectroscopy, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. In our study, the PerkinElmer Frontier FT-IR was used to identify products and establish differences in the molecular composition of liquid samples. Typically, one drop of liquid sample was put on ATR diamond glass. It scanned from  $4000\text{cm}^{-1}$  to  $380\text{cm}^{-1}$  and accumulated for 4 times for each scan. FT-IR instrument subtracts background peaks to yield the IR spectrum of the products. To use FT-IR, typical procedures were described as follows.

- 1) Pour small amount of acetone onto tissue wipers and then clean the diamond glass. Wait for 5 minutes till acetone evaporates.
- 2) Scan the background.
- 3) Use pipette to put one drop of pyrolysis oil sample on the diamond glass and scan. The result will automatically subtract the background.
- 4) Label FT-IR peaks and clean the diamond glass with acetone again. Remember to take background every time between two samples.

Analysis of FT-IR spectra at wave numbers of the pyrolysis oil provides a quick and simple qualitative technique that uses the standard IR spectra to identify the functional groups of the components of the pyrolysis oil.

## **Chapter 3: Catalytic Upgrading of Switchgrass-derived Pyrolysis Oil Using Supported Ruthenium and Rhodium Catalysts**

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### 3.1.Introduction

Due to increasing petroleum prices and a need to reduce unsustainable emission of greenhouse gases generated from burning fossil fuels, replacement of fossil fuels with renewables has drawn world-wide attention.[45] Though renewable energy sources, such as wind, solar, biomass and hydropower, can be turned into heat or electric power, a variety of biomass is the only carbon source that can be conveniently converted into liquid fuels for transportation.[46] Switchgrass as a biomass source has several advantages: 1) it is a perennial bunchgrass that requires low agricultural inputs and does not need annual reseeding, 2) the yield of dry biomass obtained from switchgrass can reach up to five tons per acre and 3) the high yield of dry biomass can meet the requirement of a secure feedstock supply, making production of commercial biofuels from switchgrass a feasible proposition.[47]

Biomass can be converted to a liquid fuel by pyrolysis in which the biomass is thermally decomposed in the absence of oxygen at an ambient pressure and a controlled temperature of 220°C or higher.[48] Under these conditions, gases, condensable volatile vapors and biochar products are produced and the volatile vapors can be condensed into pyrolysis oil (or bio-oil). To get a high yield of pyrolysis oil, a fast pyrolysis method is preferred. Fast pyrolysis involves a high heating rate and a short residence time (< 2 s) to minimize undesirable biochar and gaseous products while enhancing the pyrolysis oil yield (60-75 wt%)[48, 49]

Pyrolysis oil has a high content of oxygen (typically 35 to 50 wt%) that is present in the form of more than 300 oxygenated compounds, mainly as carboxylic acid, hydroxyketones, hydroxyaldehydes, phenolic compounds and dehydrosugars[50] that impart high polarity and high hydrophilicity. The high oxygen content results in a low heating value (less than 50% that of petroleum-derived fuels), a low pH value (2-3), high density and thermal and chemical

instability.[5] Therefore, it is necessary to upgrade pyrolysis oil to reduce its oxygen content primarily and generate a product for direct use as a fuel or chemical feedstock.

Hydrotreating is an effective option to upgrade pyrolysis oil at high temperatures (350°C to 400°C) and high hydrogen pressures (1450- 5076 psig) in the presence of a heterogeneous catalyst.[51] During catalytic hydrotreating, oxygen in pyrolysis oil is eliminated as either water or CO<sub>2</sub> by a combination of hydrodeoxygenation (HDO) and decarboxylation reactions. Large molecules in the pyrolysis oil are hydrocracked into hydrocarbons that fall in the range of hydrocarbons in diesel fuel. Many types of catalysts have been studied for their HDO activities and selectivity summarized in Table 3-1. Wildschut[5] reported experiments with Ru/C, Ru/TiO<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Pt/C, and Pd/C catalysts in a batch mode operating at 250 to 350°C under a hydrogen pressure between 1450 and 2900 psi. The highest pyrolysis oil yield (up to 60wt %) and maximum deoxygenation (up to 90wt %) were achieved by using Ru/C catalyst at 350°C and 2900 psi. Recently, Mullen and Boateng[52] reported that Ru/C and Pd/C at 320°C and 2000 psi were effective in reducing the oxygen content of pyrolysis oils from pennycress press cake. The top organic layer from hydrogenated pyrolysis oil over Ru/C had an oxygen content of 7.34 wt % (dry basis) compared with 14.65% in starting pyrolysis oil and a C/O ratio of 13.8 compared with 4.2 in raw pyrolysis oil.[52] Therefore, The Ru/C catalyst has received a lot of attention for upgrading pyrolysis oil due to its good performance for HDO. Typically, elevated temperatures and pressures of H<sub>2</sub> are required to ensure a high level of deoxygenation. However, at high temperatures, coke formation by polymerization of hydroxyphenols or methoxyphenols in pyrolysis oil has been observed as a main factor affecting the stability of catalyst.[53, 54] In addition, the catalytic upgrading under a high temperature increases the formation of CO<sub>2</sub> and CH<sub>4</sub>, which results in substantial carbon loss from the pyrolysis oil.

**Table 3- 1** Overview of catalysts investigated for catalytic upgrading of pyrolysis oil

<b>Catalysts</b>	<b>feed</b>	<b>Setup</b>	<b>Time (h)</b>	<b>P (psi)</b>	<b>T (°C)</b>	<b>DO (%)</b>	<b>O/C</b>	<b>H/C</b>	<b>Yield (wt%)</b>	<b>Ref.</b>
Co– MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	pyrolysis oil	Batch	4.0	2900	350	81	0.80	1.30	26.0	[5]
Co– MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	pyrolysis oil	Contin uous	4.0	4350	370	100	-	1.80	33.0	[55]
Ni– MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	pyrolysis oil	Batch	4.0	2900	350	74	0.10	1.50	28.0	[54]
Ni– MoS <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	pyrolysis oil	Contin uous	0.5	1230	400	28	-	-	84.0	[56]
Pd/C	pyrolysis oil	Batch	4.0	2900	350	85	0.70	1.60	65.0	[54]
Pd/C	pyrolysis oil	Contin uous	4.0	2030	340	64	0.10	1.50	48.0	[57]
Pd/C	pennycress seed pyrolysis oil	Batch	5.0(400mg pyrolysis oil ) 15.0(10g pyrolysis oil)	1987	320	-	0.05	1.70	68.3	[55]

<b>Catalysts</b>	<b>feed</b>	<b>Setup</b>	<b>Time (h)</b>	<b>P (psi)</b>	<b>T (°C)</b>	<b>DO (%)</b>	<b>O/C</b>	<b>H/C</b>	<b>Yield (wt%)</b>	<b>Ref.</b>
Pd/ZrO <sub>2</sub>	guaiacol	Batch	3.0	1160	300	-	0.10	1.30	-	[58]
Pt/ZrO <sub>2</sub>	guaiacol	Batch	3.0	1160	300	-	0.20	1.50	-	[58]
Pt/C	pennycress seed pyrolysis oil	Batch	5.0(400mg pyrolysis oil) 15.0(10g pyrolysis oil)	1987	320	-	0.21	1.50	67.1	[55]
Pt/Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	pyrolysis oil	Continuous	0.5	1230	400	45	-	-	81.0	[56]
Rh/ZrO <sub>2</sub>	guaiacol	Batch	3.0	1160	300	-	0.00	1.20	-	[58]
Ru/Al <sub>2</sub> O <sub>3</sub>	pyrolysis oil	Batch	4.0	2900	350	78	0.40	1.20	36.0	[54]
Ru/C	pyrolysis oil	Batch	4.0	2900	350	86	0.80	1.50	53.0	[54]
Ru/C	pyrolysis oil	Continuous	0.2	3335	350	73	0.10	1.50	38.0	[59]

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<b>Catalysts</b>	<b>feed</b>	<b>Setup</b>	<b>Time (h)</b>	<b>P (psi)</b>	<b>T (°C)</b>	<b>DO (%)</b>	<b>O/C</b>	<b>H/C</b>	<b>Yield (wt%)</b>	<b>Ref.</b>
Ru/TiO <sub>2</sub>	pyrolysis oil	Batch	4.0	2900	350	77	1.00	1.70	67.0	[54]
Ru/C	pennycress seed pyrolysis oil	Batch	5.0(400mg pyrolysis oil ) 15.0(10g pyrolysis oil)	1987	320	-	0.27	1.25	72.6	[55]

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In this study, Ru/C and Rh/C were selected for their well-known good hydrogenation and hydrodeoxygenation activities and Ru is known to achieve high activity toward reduction of a wide range of oxygenates. Previous studies have shown that aldehydes and ketones can react with hydrogen at 200°C to form alcohols. Olefins can be produced from dehydration of aliphatic ethers and aliphatic alcohols at 250°C and carboxylic and phenolic ether can easily react to form other oxygenated compounds at 280°C and pressures of 1600 psi or lower.[51] In the present study, the catalytic upgrading of switchgrass-derived pyrolysis oil was conducted at less severe temperatures of below 280°C to maximize carbon utilization, minimizing CH<sub>4</sub> formation and maximizing product slate.

### **3.2. Materials and methods**

#### **3.2.1. Materials**

The pyrolysis oil samples were provided by the United States Department of Agriculture (USDA)-Agricultural Research Services (ARS) in Wyndmoor, PA. The pyrolysis oil was produced from fast pyrolysis of switch grass at a feeding rate of 2.5 kg/h in a fluidized bed reactor under a nitrogen atmosphere at 500°C. The details of the pyrolysis process was described in literature.[52] Transition metal catalysts, 5 wt% Ru on C and 5 wt% Rh on C and polyethylene glycol (PEG) solvent (>99 %, mol. Wt. 380-420) were supplied by Sigma-Aldrich. Hydrogen (HP grade), Helium (UHP grade) and Compressed Air (Dry grade) were obtained from Praxair.

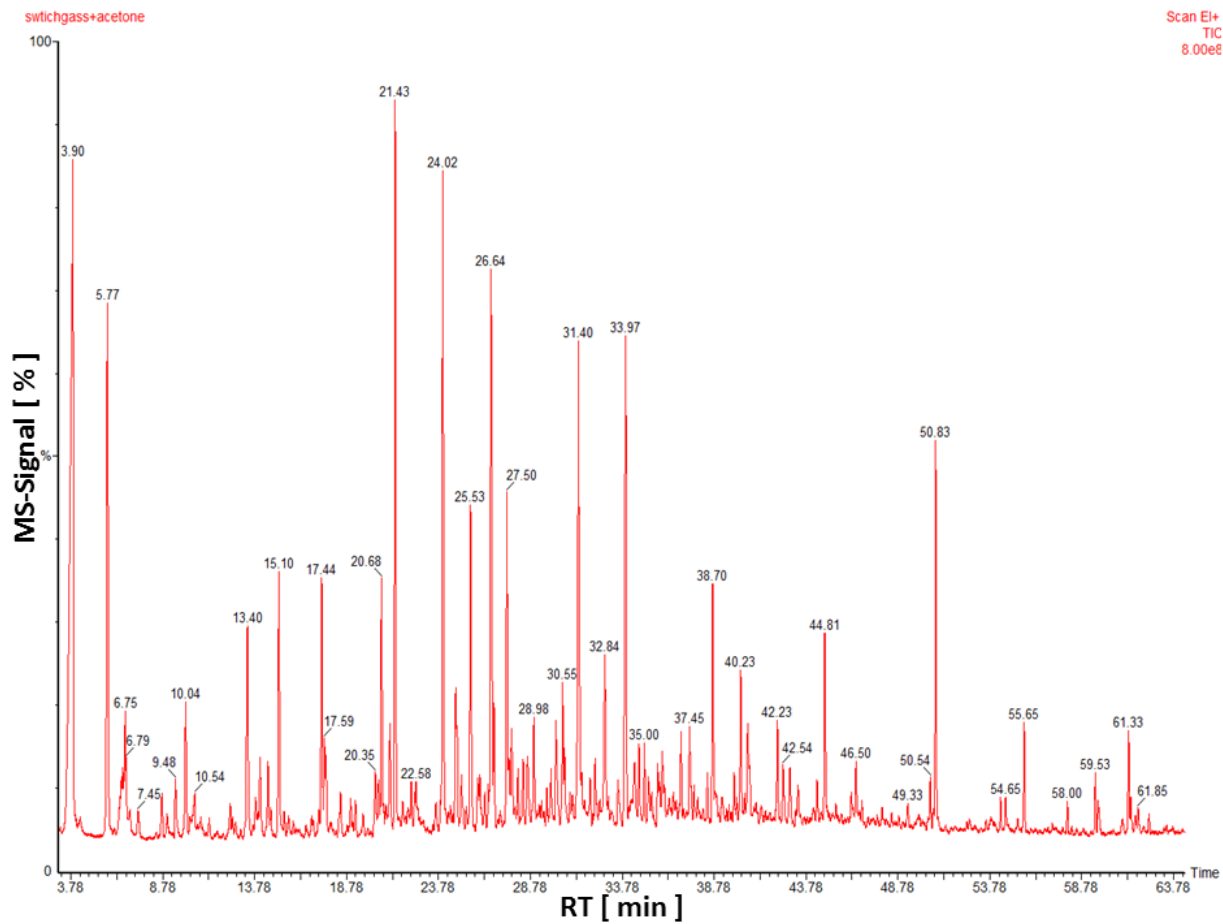
#### **3.2.2. Method**

The experimental method was same as described in the Chapter 2.

### **3.3.Results and discussion**

#### **3.3.1. Chemical composition of the crude pyrolysis oil**

The GC/MS analyses detected more than one hundred chemical compounds in the crude pyrolysis oil produced from the fast pyrolysis of switchgrass. Figure 3-1 and Table 3-2 show the chemical compounds in the crude pyrolysis oil with a peak area larger than 1% that make up about 62% of the total area. Switchgrass-derived pyrolysis oil contains many oxygenated polar components. The majority of them were phenolic compounds, which was also previously reported by others for fast pyrolysis.[60-67] Carboxylic acids, mostly formic acid and acetic acid, were also detected. They are produced from the degradation of cellulose in biomass and make pyrolysis oil corrosive. Other components in the crude pyrolysis oil included were ketones, aldehydes and small amounts of alcohols. Only pyridine was found as a nitrogen-containing compound, which showed switchgrass-derived pyrolysis oil had lower nitrogen content than other variety of biomass-derived oils. This finding is consistent with a previously reported study.[66]



**Figure 3- 1** Total ion chromatogram of a switchgrass-derived sample of pyrolysis oil used in the study

**Table 3- 2** GC/MS analysis of pyrolysis oil derived from switchgrass

<b>ID No.</b>	<b>Compound</b>	<b>Formula</b>	<b>Group</b>	<b>M<sub>w</sub></b>	<b>RT (min)</b>	<b>Area %</b>	<b>Ref.</b>
1	1-hydroxy-2-propanone	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	ketone	74	5.77	3.864	[61]
2	cyclopentanone	C <sub>5</sub> H <sub>8</sub> O	ketone	84	11.32	0.142	[60]
3	2-cyclopenten-1-one	C <sub>5</sub> H <sub>6</sub> O	ketone	82	13.40	1.738	[61]
4	2-butanone	C <sub>4</sub> H <sub>8</sub> O	ketone	72	14.51	0.503	[62, 63]
5	acetoxycetone	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	ketone	116	15.03	1.741	[62, 63]
6	3-methyl-2-cyclopentenone	C <sub>6</sub> H <sub>8</sub> O	ketone	96	17.44	1.601	[60, 61]
7	3-methyl-1,2-cyclopentanedione	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	ketone	112	24.02	3.790	
8	guaiacyl acetone	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	ketone	180	47.92	0.167	[60]
9	glycolaldehyde	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	aldehyde	60	2.28	1.059	
10	acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acid	60	3.90	10.021	[60-66]
11	n-hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	acid	256	63.51	0.060	
12	pyridine	C <sub>5</sub> H <sub>5</sub> N	nitrogen	79	9.02	0.205	[61]
13	ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	alcohol	62	6.75	0.560	[61]
14	1-hydroxy-2-butanone	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	alcohol	88	10.04	1.053	[60]
15	2-methyl furan	C <sub>5</sub> H <sub>6</sub> O	furan	98	13.40	0.050	[60]
16	furfuryl alcohol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	furan	98	14.51	0.503	[61]
17	furan	C <sub>4</sub> H <sub>4</sub> O	furan	68	19.28	0.198	[60-63]
18	4-methyl-5H-furan-2-one	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	furan	98	21.15	0.787	[60]
19	phenol	C <sub>6</sub> H <sub>6</sub> O	phenol	94	21.43	4.185	[60-66]
20	<i>o</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	25.53	2.144	[60-66]

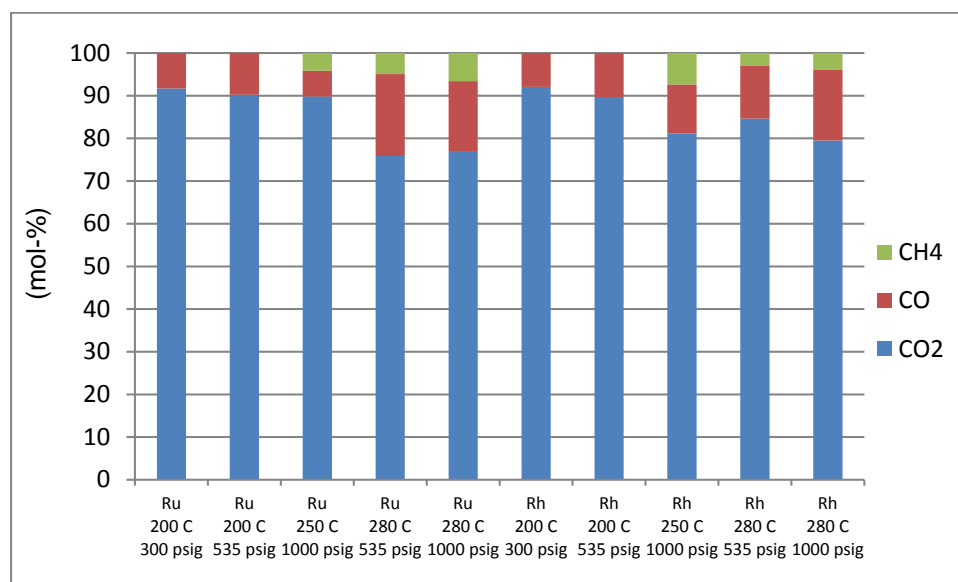
<b>ID No.</b>	<b>Compound</b>	<b>Formula</b>	<b>Group</b>	<b>M<sub>w</sub></b>	<b>RT (min)</b>	<b>Area %</b>	<b>Ref.</b>
21	<i>p</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	26.64	4.084	[60-66]
22	guaiacol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	phenol	124	27.50	1.797	[60-66]
23	2,3-dimethyl phenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	28.65	0.656	[61]
24	3-ethyl-2-hydroxy-2cyclopentenone	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	phenol	126	28.98	0.733	[66]
25	2-ethyl-phenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	29.91	0.343	[61]
26	2,5-dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	30.55	0.756	[61]
27	3,5-dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	30.64	0.425	[61]
28	4-ethyl-phenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	31.40	3.616	[61]
29	2-methoxy-4-methyl phenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	phenol	138	32.84	1.527	[61]
30	3-ethyl-5-methyl phenol	C <sub>9</sub> H <sub>12</sub> O	phenol	136	35	0.452	
31	2-methoxy-4-ethyl phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	phenol	152	36.98	0.533	[61]
32	2-methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	phenol	150	38.70	1.421	[66]
33	syringol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	phenol	154	40.23	0.896	[60-67]
34	eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	phenol	164	40.62	0.927	[60-67]
35	vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	phenol	152	42.54	0.435	[60-67]
36	methyl syringol	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	phenol	168	44.39	0.232	[60]
37	isoeugenol (trans)	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	phenol	164	44.81	1.165	[60-67]
38	acetoguaiacone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	phenol	166	46.25	0.220	[60]
39	4-propenylsyringol (cis)	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	phenol	194	52.68	0.158	[60]
40	syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	phenol	182	52.97	0.062	[60]
41	4-propenylsyringol (trans)	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	phenol	194	54.65	0.237	[60]

ID No.	Compound	Formula	Group	M <sub>w</sub>	RT (min)	Area %	Ref.
42	acetosyringone	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	phenol	196	55.65	0.639	[60]
43	2,3-dihydrobenzofuran	C <sub>8</sub> H <sub>8</sub> O	aromatic	120	33.97	3.651	[61]
44	1,2,3-trimethoxy-5-methylbenzene	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	aromatic	182	47.65	0.073	[67]
45	hexadecane	C <sub>16</sub> H <sub>34</sub>	hydrocarbon	226	50.83	2.177	

Abbreviations: M<sub>w</sub>, molecular weight; RT, retention time; Ref, references (these compounds were also identified by others)

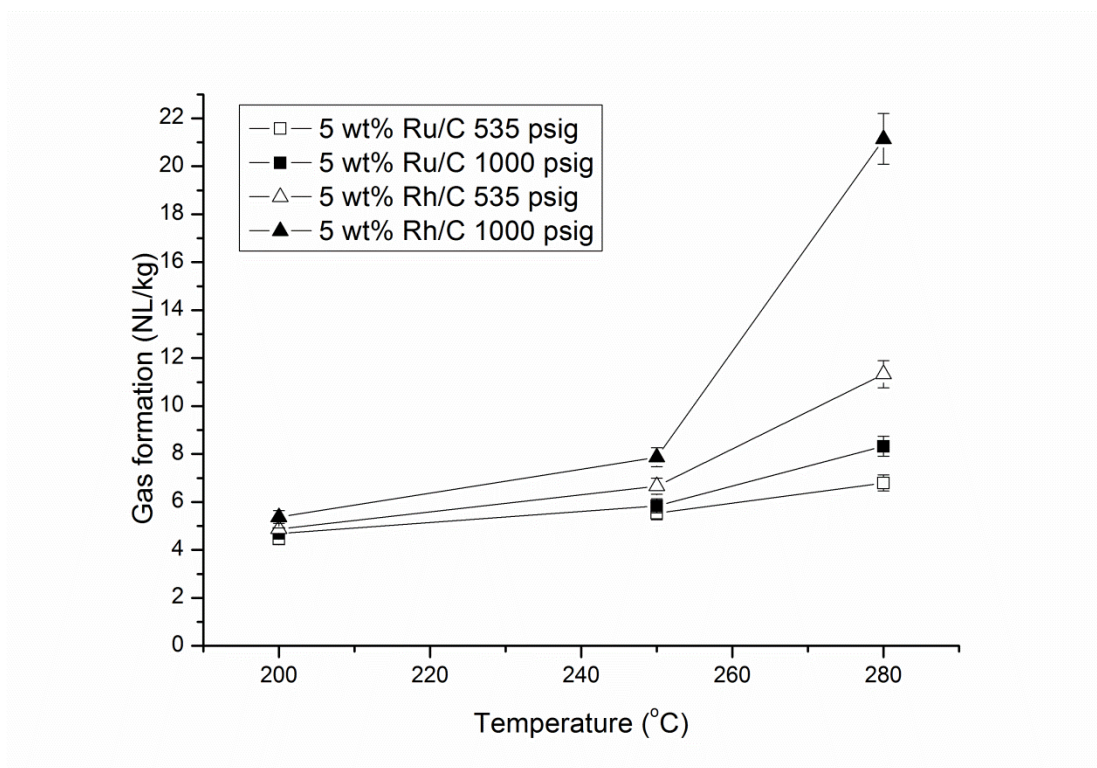
### 3.3.2. Effect of catalysts on the distribution of gas products

The majority (90–99%) of the gas collected at the end of the upgrading experiments was unreacted H<sub>2</sub>, indicating the reactions were performed under a hydrogen-excess condition. Fig. 3-2 shows the composition of the non-condensable by-product gas generated during upgrading.



**Figure 3- 2** Composition of gas by-product from the HDO reaction of switchgrass pyrolysis oil over Ru/C and Rh/C catalysts under different temperature and pressure

CO<sub>2</sub> was a dominant component in the gaseous product, which was 70–90% of the product gas. It is known that CO<sub>2</sub> is mainly produced from the decarboxylation of organic acids while CO is produced from decarbonylation and water gas shift reaction. CH<sub>4</sub> was only found when the operating temperature was above 250°C. Because CH<sub>4</sub> formation contributes to the reduction of the C/H ratio, it is an undesired gas byproduct. Other gaseous species were ethane, propene and propane but their contents were small (< 0.01%). These gases might be generated due to hydrocracking.



**Figure 3- 3** Effect of temperature and hydrogen pressure on gaseous product formation during HDO with the catalysts of Ru and Rh supported on carbon

Fig. 3-3 shows the effects of temperature and hydrogen pressure on the formation of gases during the HDO with Ru/C and Rh/C catalysts for 5 hours. In general, the upgrading with Rh/C produced more gas than the one with Ru/C. At a low temperature (e.g., 200°C), the gas yields were relatively low (i.e., 4-6 Normal liter/kg) for both catalysts. However, the amount of gas generated

increased with temperature as gaseous components such as ethane, propene and propane were produced by hydrocracking of larger hydrocarbons in starting pyrolysis oil at a high temperature.[52]

The highest amount of gas was 21.14 NL/kg of pyrolysis oil, which was obtained by the catalytic HDO with the Rh/C at 280°C and 1000 psig. However, the yield of gas decreased to 11.33 NL/kg when the hydrogen pressure was reduced to 535 psig. The upgrading with Ru/C followed the same trend. Fig. 3-2 shows that most of the gas product was CO<sub>2</sub>. The CO<sub>2</sub> was produced partly from decarboxylation of organic acids in the pyrolysis oil. Wildschut[45] found that CO<sub>2</sub> might be formed from D-glucose in pyrolysis oil during HDO over Ru/C. During the HDO, glucose in pyrolysis oil could be catalytically converted to levulinic acid and formic acid, which could be further decarboxylated to produce CO<sub>2</sub>. In this study, Rh/C exhibited the same catalytic selectivity for the CO<sub>2</sub> formation. So increasing H<sub>2</sub> pressure may shift the thermodynamics further towards complete conversion of glucose and would result in the production of more CO<sub>2</sub>.

**Table 3- 3** Mass balance and yields during HDO at different temperatures and pressures

(values in wt %)<sup>1</sup>

catalyst P (psig)	Ru/C						Rh/C						Baseline <sup>2</sup>
	535			1000			535			1000			1000
T (°C)	200	250	280	200	250	280	200	250	280	200	250	280	280
Liquid	88.4	94.2	86.2	78.4	95.1	85.5	86.3	89.2	84.7	85.0	92.2	88.8	94.3
Gas	1.8	2.2	2.9	1.8	2.3	3.3	2.0	2.3	4.1	2.2	2.4	5.3	1.5
Solid	1.5	1.5	2.2	0.6	0.8	2.3	0.5	0.9	1.1	0.4	0.5	0.5	0.3
closure	91.7	97.9	91.3	80.8	98.2	91.1	88.8	92.4	89.9	87.6	95.1	94.6	97.6

<sup>1</sup>Error: ±5%; <sup>2</sup>No catalyst

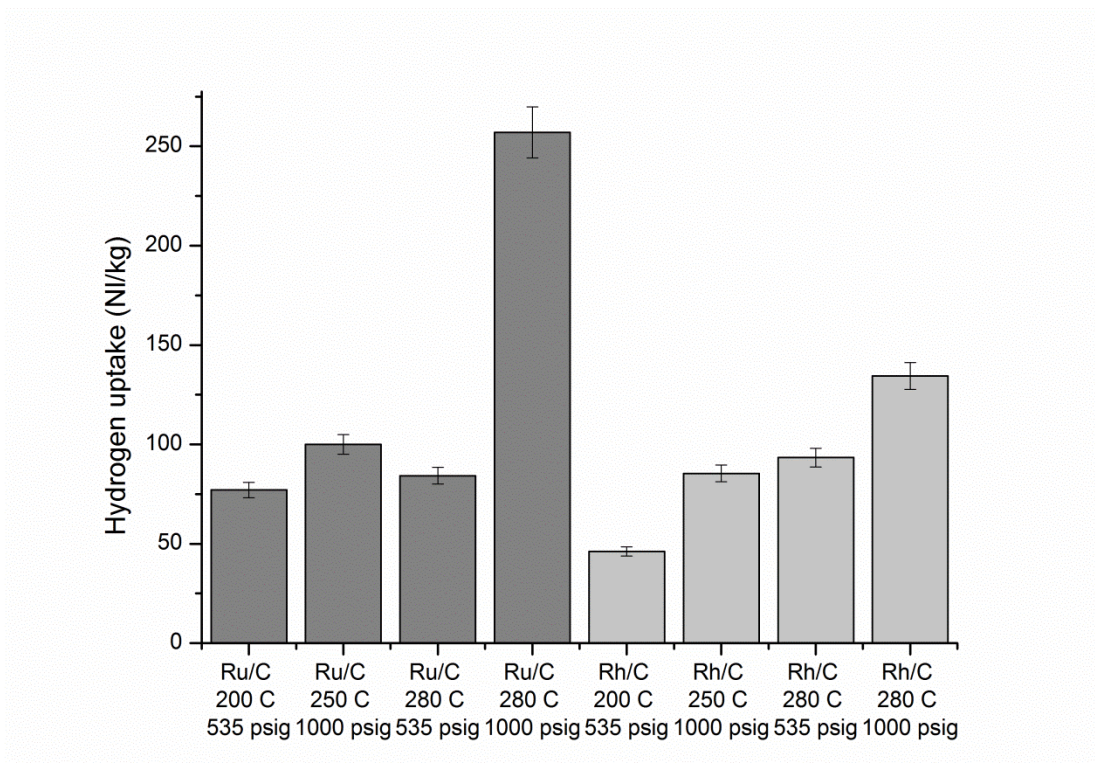
All product yields were calculated based on the mass balance. Liquid samples were weighed before and after experiments. Since PEG-400 didn't participate in reaction, it could be treated as inert substance. Therefore, the liquid product yield was calculated by subtracting PEG and solid



weight from final total sample weight. After recovering liquid samples, acetone was used to rinse the reactor and then filtered by filter paper. Subsequently, the filter paper was dried in the oven and weighed. The weight of solid minus original catalyst used was the solid formed during HDO reaction. Gas yields were based on its composition determined by GC.

The total mass of the three products collected in the experiments was typically between 81-98 wt% as shown in Table 3-3. Runs with low mass balance (i.e., <95%) was likely caused by the evaporation of volatile compounds during work-up of the products. The liquid yield increased with temperature (from 200 to 250°C), likely due to increase in the HDO/hydrogenation rates and hence increased production of water and other products. However, when the temperature was raised to 280°C, the liquid yield decreased slightly. The reactor contained solid at the bottom of the vessel after reaction, likely as a result of polymerization in the presence of a catalyst. The solid ranged from 0.5 wt% to 2.3 wt% of the total sample weight, indicating that the mild experimental conditions reduced coke formation. For runs in the absence of a catalyst (baseline run), the data show that only 22 NL/kg H<sub>2</sub> was consumed, demonstrating that H<sub>2</sub> consumption was low when a catalyst was not utilized. Only a small amount (0.3 wt%) solid was formed in the latter case.

### 3.3.3. Effect of process parameters on hydrogen consumption



**Figure 3- 4** Effects of temperature and pressure on H<sub>2</sub> consumption in the hydrotreatment of pyrolysis oil with Ru/C and Rh/C catalysts

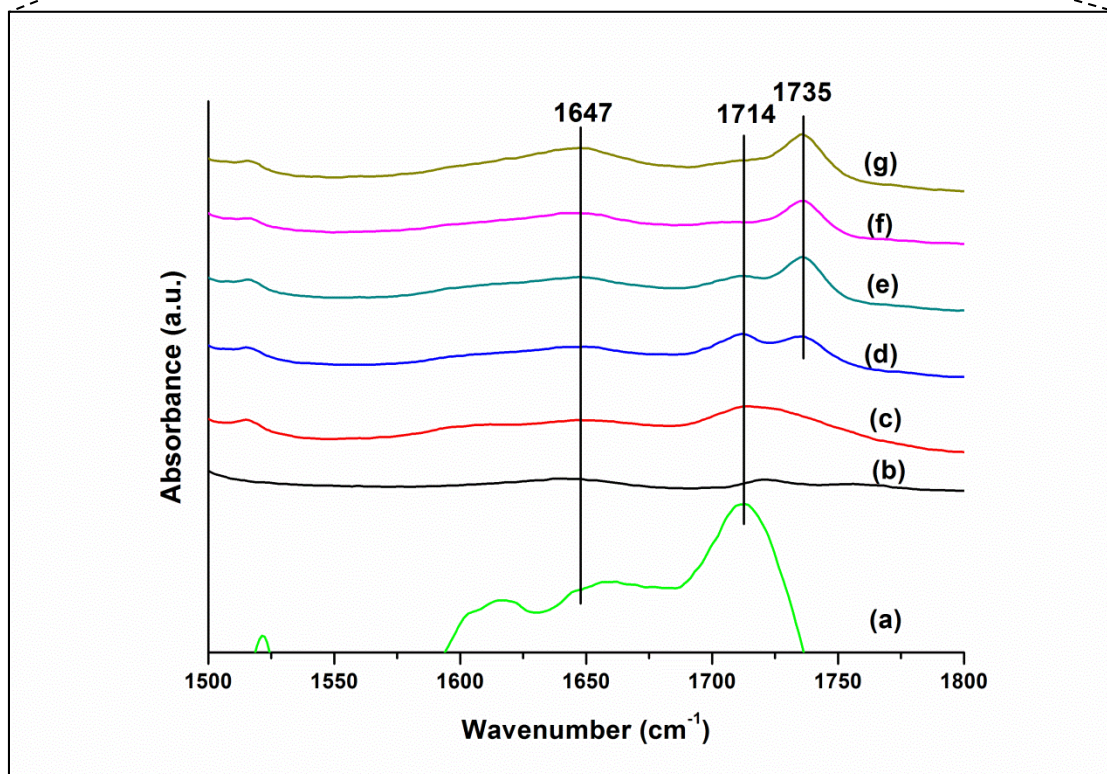
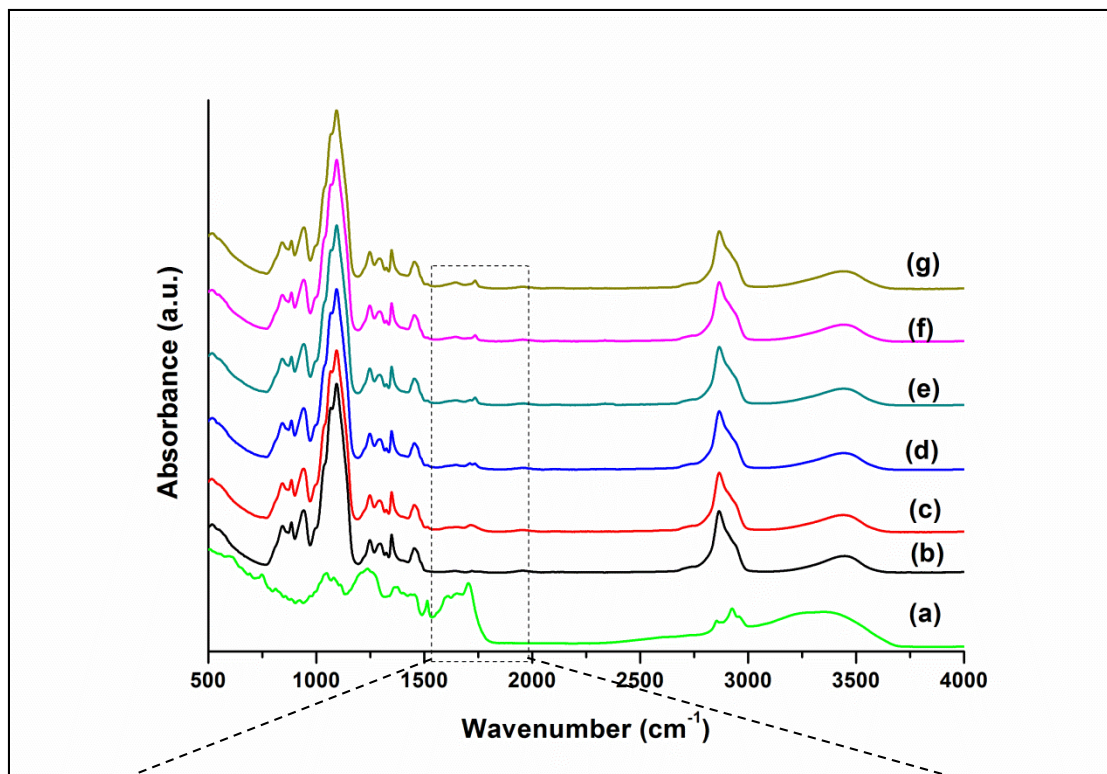
Fig.3-4 gives the amounts of hydrogen consumed during HDO under different conditions. Hydrogen consumption was measured by the following steps: 1) Calculating pressure drops before and after experiments at same room temperature measured by pressure gauge. 2) Hydrogen percentage after experiment was tested by GC. 3) Using ideal gas law, total mole of hydrogen consumption was calculated.

As shown in Fig. 3-4, the amount of hydrogen used for Ru/C was higher than that for Rh/C. The hydrogen consumption was 257 NL per kg of pyrolysis oil when using Ru/C at 280°C, and 1000 psig. The reaction catalyzed with Rh/C under the same experimental conditions consumed about 134 NL/ kg of pyrolysis oil. Most of hydrogen used was to generate H<sub>2</sub>O via HDO. The second large portion of H<sub>2</sub> usage during hydrogenation was to saturate C-C double bonds in the

aromatic rings. Another pathway for hydrogen consumption is methanation. However, methane yields were extremely low in our experiments. Higher hydrogen consumption is expected to favor higher H/C ratios, leading to higher heating value (HHV). As the temperature increased, the H<sub>2</sub> consumption increased as well. An explanation is that both Ru/C and Rh/C catalysts were more active at higher temperature for the HDO reaction. Increasing H<sub>2</sub> pressure also led to higher hydrogen consumption. This is because higher pressure keeps water in the pyrolysis oil in a liquid state, which can promote the solubility of H<sub>2</sub> in the polar pyrolysis oil for an increase in the rate of the hydrogenation reactions. It is also well known that a high pressure of hydrogen reduces coke formation, thereby maintaining the catalyst activity during the course of the experiment.

#### **3.3.4. FT-IR data**

Fig.3-5 shows the comparison of the FT-IR spectra of raw and upgraded pyrolysis oil over Ru/C at different temperatures and pressures. The majority of peaks were from the solvent, PEG-400 that contains significant amounts of C-C, C-O and O-H groups to impart its polarity and make it fully miscible with the pyrolysis oil. However, the functional groups in the solvent PEG-400 (Pyrolysis-oil: PEG = 1: 9) exhibited sharp and relatively high intensity peaks that resulted in masking peaks from the products. However, some differences of peaks of spectra could be discerned between 1500 cm<sup>-1</sup> to 1900 cm<sup>-1</sup> wavenumbers.



**Figure 3- 5** A comparison of the FT-IR spectra of raw and upgraded pyrolysis oil (a) Raw Switchgrass Pyrolysis Oil (b) PEG-400 solvent (c) Raw Pyrolysis Oil (90%) in PEG-400 (10%) by volume (d) Upgraded Pyrolysis Oil with PEG 200°C, 535 psig (e) Upgraded Pyrolysis Oil with PEG 250°C, 1000 psig (f) Upgraded Pyrolysis Oil with PEG 280°C, 535 psig (g) Upgraded Pyrolysis Oil with PEG 280°C, 1000 psig

The peak at  $1714\text{ cm}^{-1}$  is associated with the C=O group in carboxylic acids and in raw pyrolysis oil, the intensity of this peak was the highest.[68] Most of carboxylic acids in the pyrolysis oil were acetic acid that accounted for 3.85 wt% in the raw pyrolysis oil (qualitatively confirmed by GC). As the temperature increased from 200°C to 280°C, the intensity of C=O stretching vibration peak decreased steadily. At 200°C, the upgraded pyrolysis oil sample still had 2.54 wt% acetic acid. However, when the temperature reached 280°C, the peak disappeared as most of carboxylic acids, a major contributor to the pyrolysis oil corrosiveness, was removed. One of the possible pathways observed was decarboxylation, which removed O from the pyrolysis oil as CO<sub>2</sub>. The increased hydrogen pressure from 535 psig to 1000 psig had no significant effect on the conversion of the C=O bond in carboxylic acids. Similar results were reported in literature [69] for conversion of organic acids under a high-pressure thermal treatment in the absence of hydrogen and catalysts to CO<sub>2</sub> at elevated temperatures (250-350°C).

After the HDO treatment of the raw pyrolysis oil, a new band appeared at  $1735\text{ cm}^{-1}$  that was the C=O stretching vibration band in ketones or ester group.[70] The intensity of the C=O peaks increased with temperature. In addition to the decrease of carboxylic acid in the original pyrolysis oil sample via CO<sub>2</sub> evolution, another likely pathway for the acid reduction was the esterification of formed alcohols and carboxylic acids that could easily occur at a mild temperature. A control group of experiments conducted using C<sub>30</sub> hydrocarbons as a solvent confirmed the same new ester C=O stretching vibration peak in upgraded pyrolysis oil. This evidence demonstrated that the alcohols that reacted with carboxylic acids were from pyrolysis oil rather than from the PEG-400 solvent.

The peaks at  $1647\text{ cm}^{-1}$  represent the C=C stretching vibration of alkenes.[68] From the GC/MS data, alkenes were found in the crude pyrolysis oil. The intensity of this peak increased as temperature increased particularly when temperature was above  $250^{\circ}\text{C}$ . The FT-IR data are consistent with higher hydrogen consumption at elevated temperature due to dehydroxylation of phenolic compounds to produce alkylbenzenes.

### **3.3.5. GC/MS profiles of the upgraded pyrolysis oil**

GC/MS analysis was used to investigate the effect of the catalyst used on the changes of the main products in the upgraded pyrolysis oil. Esters such as ethyl acetate, formic acid ethyl ester and propanoic acid propyl ester were found after upgrading, which was in agreement with the FT-IR results. Table 3-4 presents the most abundant and valuable compounds classified according to their functional groups in the upgraded pyrolysis oil. Generally, the most abundant compounds in the upgraded products were aromatics, phenols, aliphatic and aromatic hydrocarbons. The phenolics were most likely products of the HDO of the lignin fraction in the pyrolysis oil. The major components in this group were methylated, ethylated and propylated phenolics. Cyclic derivatives were quantified in upgraded samples (3-5 area %). They were formed by subsequent reactions of the phenolics and alkylbenzenes with hydrogen. Substantial amounts of aliphatic hydrocarbons and alkylbenzenes such as hexadecane, 3-nonene and 1-benzyl-3-ethylbenzene were identified in mass spectrum. The highest relative concentration of hydrocarbons for Ru and Rh catalysts were 19.9% and 21.2% individually. Aldehydes and ketones disappeared after hydrotreating, and alcohols such as propylene glycol, ethylene glycol, cyclopentanol were formed. Ru/C showed better alcohols selectivity (5.2%) than Rh/C (0.9%) at the same conditions. Ru/C gave better selectivity for alcohols production than Rh/C but both Ru and Rh based catalysts had a potential to provide higher yield of hydrocarbons.

Other hydrocarbon products in upgraded pyrolysis oil after solvent fractionation were also analyzed by GC/MS and they were mainly cyclohexane and methyl-cyclopentane. These compounds were likely formed by the HDO of phenolics.

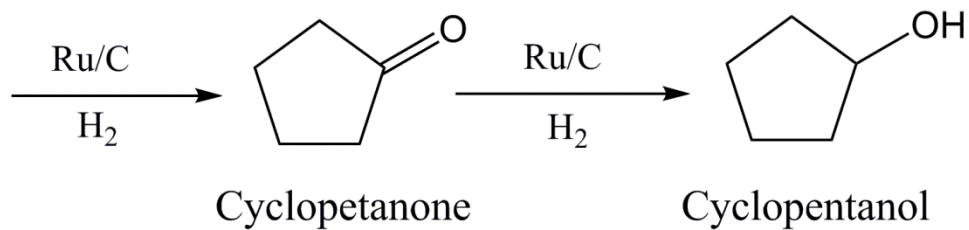
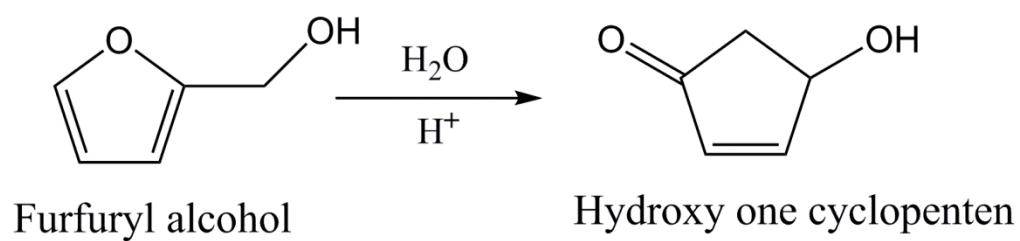
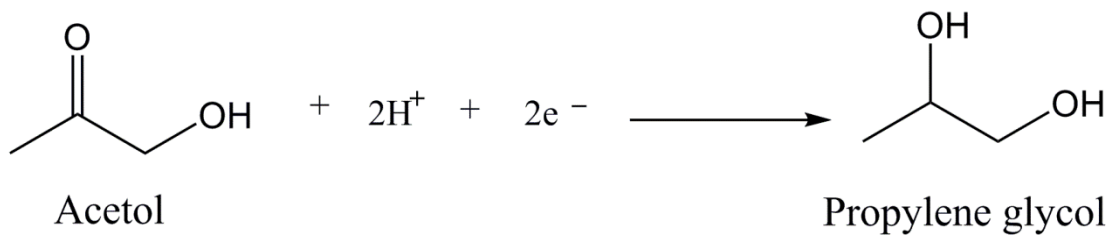
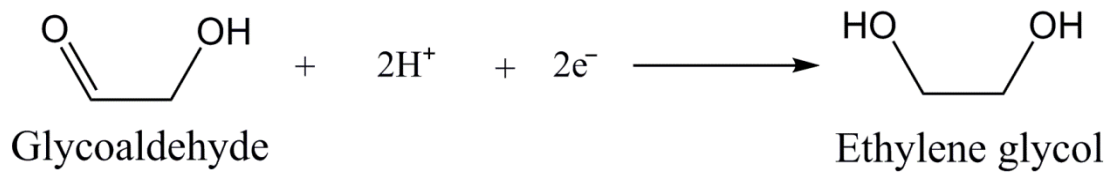
**Table 3- 4** Individual compounds of selected component classes in upgraded pyrolysis oil produced using a Ru/C and Rh/C catalyst (280°C, 1000 psig)

Compound	Group	Relative area percentage (%)	
		Rh/C 280°C	Ru/C 280°C
Phenol	Phenolics	7.951	8.377
2-methyl phenol	Phenolics	3.214	3.034
p-cresol	Phenolics	6.777	6.252
2-methoxy phenol	Phenolics	4.180	3.093
2,4-dimethyl phenol	Phenolics	1.320	1.327
2,6-dimethyl phenol	Phenolics	1.555	1.161
2-methoxy-4-propyl phenol	Phenolics	13.385	12.481
cyclohexanone	Cyclic compounds	4.308	3.051
2-methyl cyclopentanone	Cyclic compounds	*	*
cyclopentanone	Cyclic compounds	1.332	-
4-ethyl cyclohexanone	Cyclic compounds	-	0.737
propanol	Alcohols	-	0.498
ethylene glycol	Alcohols	0.861	1.744
propylene glycol	Alcohols	-	1.752
cyclopentanol	Alcohols	-	1.212
methyl cyclopentane	Alkanes	*	*
propyl cyclopentane	Alkanes	1.085	1.256
cyclohexane	Alkanes	*	*
hexadecane	Alkanes	4.720	6.595
3-nonene	Alkanes	-	0.462
2-propenyl benzene	Alkylbenzenes	0.548	0.892
1-benzyl-3-ethylbenzene	Alkylbenzenes	13.625	11.980

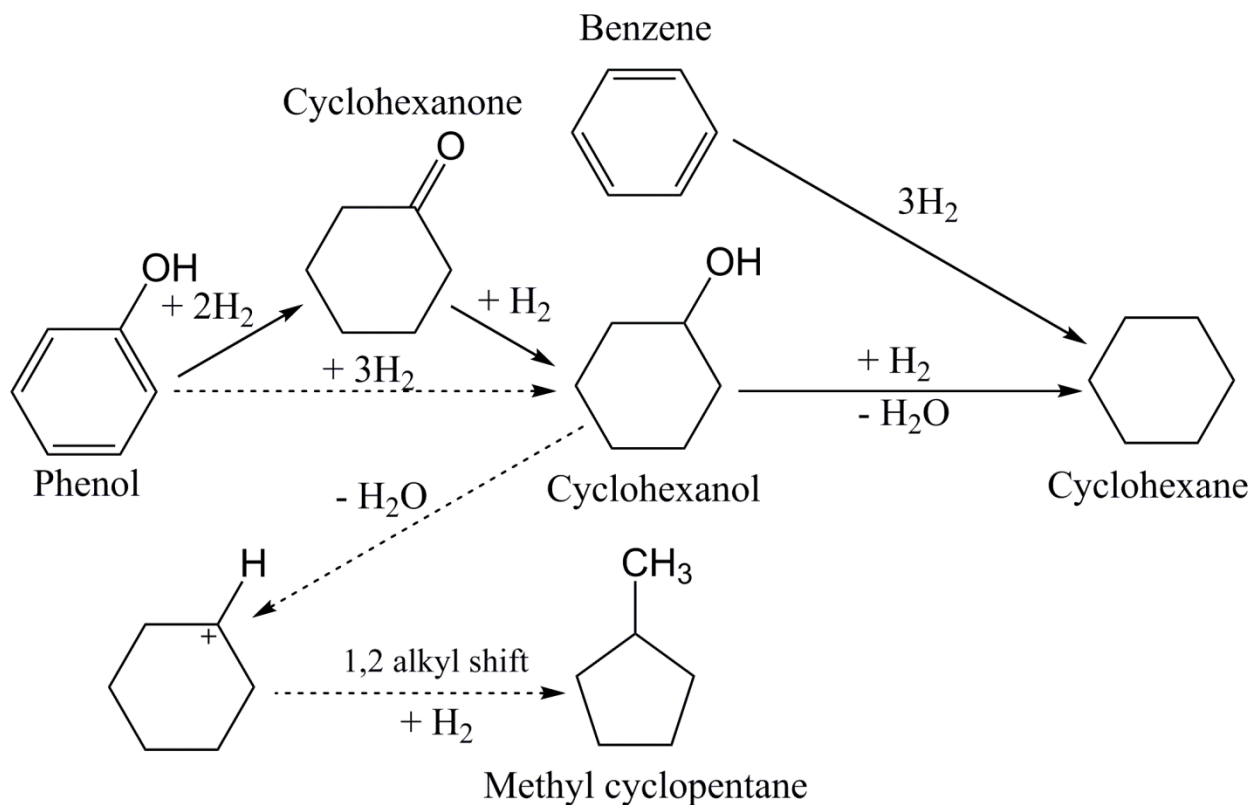
\*Solvents extraction fractions

### 3.3.6. Proposed reaction mechanisms for alcohols and hydrocarbons formation during hydrotreating of pyrolysis oil

Fig.3-6 shows the possible mechanism for the formation of the alcohols and hydrocarbons in the upgraded pyrolysis oil.







**Figure 3- 6** Possible reaction paths for hydrogenation of switchgrass pyrolysis oil to form alcohols and hydrocarbons (Solid arrow indicates the main route to products)

Phenol was mainly converted to cyclohexanol. Fig. 3-6 shows a reaction mechanism for hydrogenation of the aromatic ring that occurs as a first step followed by deoxygenation, with cyclohexanol as the intermediate product and cyclohexane as the final product. However, both cyclohexanol and cyclohexane were observed in small amounts and could only be detected in solvent extraction fractions. In addition, cyclohexanone was found in relatively large amount in final products. This phenomenon suggested that hydrogenation of phenol over Ru/C and Rh/C produced cyclohexanone as the primary product. Shuikin and Erivanskaya[71] have made the same conclusion from the data for the pyrolysis oil upgraded with Ni based catalysts. Methyl cyclopentane was also found in hexane solvent extraction portion indicating another route, in which cyclohexanol could be dehydrated to cyclohexyl cation and then converted to methyl cyclopentane with 1, 2 alkyl shift at mild temperature.

In our upgrading of the pyrolysis oil at mild conditions, a mixture of alcohols such as ethylene glycol, propylene glycol and cyclopentanol were produced. From the GC/MS data in Table 3-2, acetol and glycolaldehyde had fully disappeared after upgrading. Possible reaction pathways are shown in figure 3-6. Besides diols production, other alcohols such as ethanol, 2-propanol and 2-butanol were produced in small quantities in the upgraded samples.

In terms of the concept of HDO of pyrolysis oil over Ru/C and Rh/C catalysts, H<sub>2</sub> was adsorbed and activated on metal sites. In the meantime, oxygenated compounds were adsorbed also on noble metal sites or activated carbon interface. Then, the H<sub>2</sub> dispersed on catalyst reacted with oxygenated compounds intermediates resulting in the cleavage of C-O bonds to form H<sub>2</sub>O and deoxygenated compounds. In HDO experiments, catalysts played an important role of transition state modification to lower the activation energy of HDO reaction.

### 3.3.7. Catalysts stability

The recyclability of Ru/C catalyst in hydrodeoxygenation of switchgrass-derived pyrolysis oil was examined by recharging the reactor with H<sub>2</sub> four times (Table 3-5). In the four charges, the H<sub>2</sub>/Ru mol ratio was 1031, 916, 1073, 642, respectively. A total of over 3600 cycles in Ru showed that the system was catalytic in Ru and it remained active during HDO processing.

**Table 3- 5** Reuse of Ru/C in hydrodeoxygenation of switchgrass-derived pyrolysis oil

*Run	Catalysts	Temp eratur e (°C)	P(initial) (Psig)	P(final) (Psig)	ΔP (Psig)	Products Gas Composition			
						CO <sub>2</sub> %	CO %	H <sub>2</sub> %	H <sub>2</sub> /Ru (mol ratio)
Charge1	Ru/C	200	1000	976	24	0.486	0.073	96.25	1031
Charge 2	Ru/C	200	1002	972	30	0.344	0.106	97.55	916
Charge 3	Ru/C	200	1003	977	26	0.461	0.056	96.21	1073

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Charge 4	Ru/C	200	1000	984	16	0.211	_	97.79	642
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\*5 hours runs. In each run, the Ru/C loading was 0.1g, of which Ru was 0.005g.

### 3.4.Conclusions

The switchgrass-derived pyrolysis oil was upgraded over 5 wt% Ru/C and 5 wt% Rh/C catalysts slurried with polyethylene glycol under mild temperatures of 200- 280°C and pressures of 300-1000 psig. The highest gas yield of HDO of pyrolysis oil was 17.1 NL/kg and the gas phase generated during upgrading had 70-85% CO<sub>2</sub>, which indicated that the oxygen in the pyrolysis oil was removed. An increase in reaction temperature led to an increase in the yield of gaseous phase and a decrease of the acetic acid content in the oil phase, from 3.85 wt% to below 0.01 wt%. According to the amount of gas formed, hydrogen consumption level and composition of oil products, both Ru/C and Rh/C catalysts appear to be promising. Gas analysis of the upgraded pyrolysis oil showed that Rh/C was more effective for CO<sub>2</sub> formation and Ru/C had higher hydrogen consumption. FT-IR data reveals that the esterification reaction took place, which indicates more alcohols were possibly produced and reacted with carboxylic acids. The alkene C=C stretching vibration was also found in the IR data of the upgraded pyrolysis oil showing that hydrocarbons were produced during HDO. The GC-MS data demonstrates that the highest HDO activity of switchgrass pyrolysis oil was obtained with Ru/C at 280°C and 1000 psig. The main products included 5.2% alcohols, 3.8% cyclic compounds, 21.2% hydrocarbons and 35.7% phenolics. Results show a potential method for upgrading pyrolysis oil into a stable fuel at mild conditions.

**Chapter 4: Hydrodeoxygenation of Fast-pyrolysis Pyrolysis oils From Corn Stover and Soybean Straw Using Heterogeneous Catalysts**

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#### **4.1.Introduction**

Transportation fuel consumption is becoming a major concern due to the increase in demand caused by the growing human population. The main concerns surrounding transportation fuels are the limited fossil fuel resources, the emission of CO<sub>2</sub> created from combustion and the increase in fuel demand. Extensive research is being conducted on alternative fuels suitable to replace fossil fuels reducing the concerns listed above. Biomass is considered to be a major potential renewable resource. In the previous chapter, we discussed the study of upgrading switchgrass derived pyrolysis oil into hydrocarbon or alcohol fuels. In this chapter results and discussion regarding HDO of corn stover and soybean straw pyrolysis oil will be given.

Nowadays, industrial biomass uses in primarily of agricultural residues, forest products, urban and industrial residues. At 23 mt/year, corn stover (including stalks, leaves and husks without cobs) has become the largest quantity of agricultural crop biomass produced in the United States.[72, 73] So, it is considered a potential cellulosic feedstock for biofuels production. Soybean is a leguminous crop. The worldwide annual production of soybean is estimated to be about 120 million tons, 47% of which is generated in the United States. Soybean oil has been widely studied as a starting material for fatty acid methyl ester (biodiesel) production by trans-esterification.[74, 75] Beside soybean, soybean straw after agriculture harvest provided huge biomass potential to generate cellulosic derived biofuels. However, harvesting of corn stover and soybean straw from field has negative environmental effects including decrease in soil organic carbon and soil's ability to retain water.[72] Lal has reported that removal of even as little as 25% of corn stover from some soils can have major detrimental effects.[76] Pyrolysis, unlike other biochemical conversion, can convert partial biomass to produce biochar, which can be left in the farm field to build the soil and

sequester carbon.[77] Moreover, biochar returns the plant nutrients to the soil thus allowing more biomass removal.

As mentioned in Chapter 2, pyrolysis oil contains a large amount of oxygen that results in more than 300 compounds that make it thermally and chemically unstable. Upgrading of pyrolysis oil is necessary. In this study, the discussion is based on the effects of catalysts, and HDO temperature on the product yields and its composition. The pyrolysis oil was characterized for physical properties and detailed chemical composition. The chemical composition of pyrolysis oils were analyzed using a combination of chromatographic and spectroscopic techniques.

## **4.2. Materials and methods**

### **4.2.1. Materials**

The pyrolysis oil samples were provided by the United States Department of Agriculture (USDA)-Agricultural Research Services (ARD) in Wyndmoor, PA. Transition metal catalysts, NiCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CoCl<sub>2</sub>, Ru (bipy)(CO)<sub>2</sub>Cl<sub>2</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, polyethylene glycol (molecular weight: 400), Hexadecane were obtained from Sigma-Aldrich. Ru/C and Rh/C was obtained from Engelhard Minerals & Chemicals Corporation and polyethylene glycol (PEG) solvent (>99 %, mol. Wt. 380-420) were supplied by Sigma-Aldrich. Hydrogen (HP grade), Helium (UHP grade) and Compressed Air (Dry grade) were obtained from Praxair.

### **4.2.2. Method**

The experimental method was as described in Chapter 2.

### **4.3.Results and discussion**

#### **4.3.1. Characterization of corn stover and soybean straw pyrolysis oil samples**

Table 4-1 explains the definition of various parameters related to pyrolysis oils and the associated ASTM analytical methods. The properties of corn stover and soybean straw-derived pyrolysis oil are listed in Table 4-2.

The pH value of the samples was measured using an Oyster-10 pH/mV/Temperature Meter (Extech Instruments). The pH of 2.41 was observed for soybean straw derived pyrolysis oil, while corn stover oil showed a pH of 2.37. Due to the acids content in the pyrolysis oil, pH value of the samples were much lower than petroleum based fuels. The acidity of the samples causes a major concern as its use for potential fuel source. The pour point was investigated using a K46100 Cloud Point & Pour Point Apparatus (Koehler Instrument, Inc). The pour point of the corn and soy samples is calculated to be  $-19^{\circ}\text{C}$  and  $-17^{\circ}\text{C}$  respectively. This falls well in the range of observed pour points of  $-13^{\circ}\text{C}$  to  $-33^{\circ}\text{C}$ . The density of the pyrolysis oils was measured at  $25^{\circ}\text{C}$  for the corn (1.2310 g/ml) and soy (1.1749 g/ml) sample. When compared to density of light fuel oil (0.85 g/ml), density of pyrolysis oils is much greater.

Kinematic Viscosity is measured at  $40^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  using a calibrated capillary viscometer (Koehler Instrument, Inc). The corn sample is observed to have a higher viscosity than soy. At  $40^{\circ}\text{C}$  the viscosity of corn is measured at  $15.24\text{ mm}^2/\text{s}$  meanwhile, the viscosity of soy is measured at  $10.89\text{ mm}^2/\text{s}$ . A drastic drop in viscosity is noted when measured at  $100^{\circ}\text{C}$ . The viscosity of corn is measured at  $2.41\text{ mm}^2/\text{s}$ , while that of soy is read at  $1.81\text{ mm}^2/\text{s}$ . At higher temperatures the viscosity of both samples is relatively close to each other. Meanwhile, at lower temperatures, the difference between the viscosities is larger. This plays an important role in the storage of the pyrolysis oil. Soy could potentially be easier to handle in terms of storage than corn. The results

from composition testing showed a larger amount of unwanted oxygen in both the samples. Reduction in oxygen is essential in order to increase energy density and miscibility with hydrocarbon fuels.

**Table 4- 1** List of pyrolysis oil parameters to establish the quality of fuel

<b>Parameter</b>	<b>Units</b>	<b>Description</b>	<b>Analytical Method</b>
Flash Point	°C	Lowest temperature the vapor above the liquid can be ignited with an open flame.	ASTM D93
Pour Point	°C	Lowest temperature at which the liquid can flow without disturbance.	ASTM D97
Cloud Point	°C	The highest temperature at which crystallization of waxy materials appear in the liquid.	ASTM D2500
Density(25°C)	Kg/L	Mass per unit volume.	ASTM D4052
Acidity	pH		pH meter
Kinematic Viscosity	cSt	Resistance of a fluid which is being deformed by shearing or strain stress.	ASTM D445
Ash	wt%		ASTM D482
Compatibility		Mixture of bio-fuel and diesel	ASTM D4740
Water content	wt%		ASTM D203
Heating value	MJ/kg	Energy per unit mass	DIN 51900

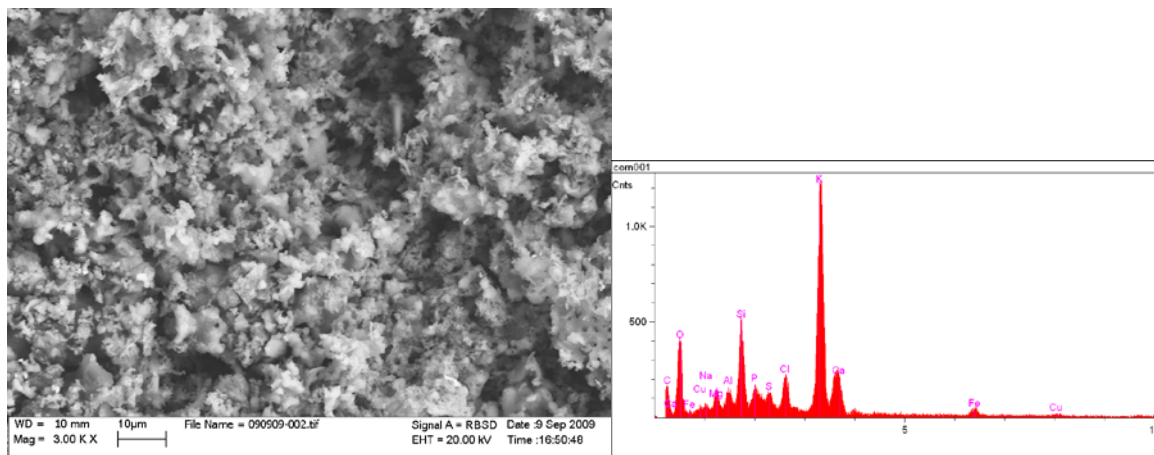


**Table 4- 2** Properties of pyrolysis oils derived from two biomass crops

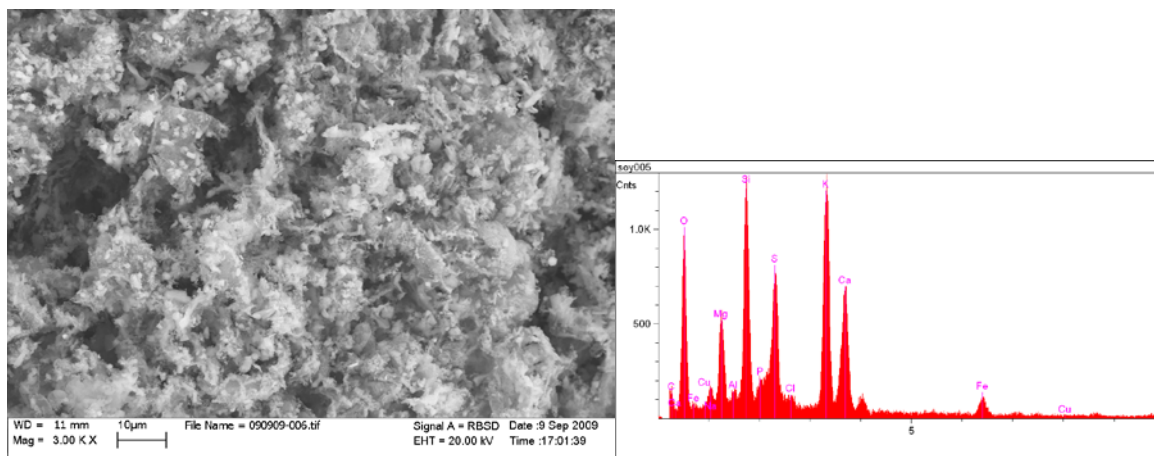
<b>Physical Property</b>	<b>Corn stover</b>	<b>Soybean straw</b>
Stability	Unstable	Unstable
pH	2.37	2.41
Viscosity (cSt)		
@ 40°C	15.24	10.89
@ 100°C	2.41	1.81
Pour Point (°C)	-19	-17
Density (@ 25°C) Kg/l	1.23	1.17
Ash (wt%)	0.05	0.06
Carbon (wt%)	40.81	42.64
Oxygen (wt%)	51.21	49.54
Hydrogen (wt%)	7.29	6.94
Sulfur (wt%)	0.15	0.14
Nitrogen (wt%)	0.54	0.74

The ash content of pyrolysis oil is measured by heating the pyrolysis oil in an electric heater. The pyrolysis oils were heated to 500°C to insure all light elements are evaporated, because ash content is mostly composed of heavier elements. Figure 4-1 depicts the chemical and physical makeup of the ash under the SEM. High levels of potassium (K), calcium (Ca), silicon (Si) and oxygen (O) are also observed in XRD spectrum of pyrolysis oil the samples. The soy sample clearly shows a larger quantity of heavier elements as compared to corn (Figure 4-1 b).

(a)



(b)

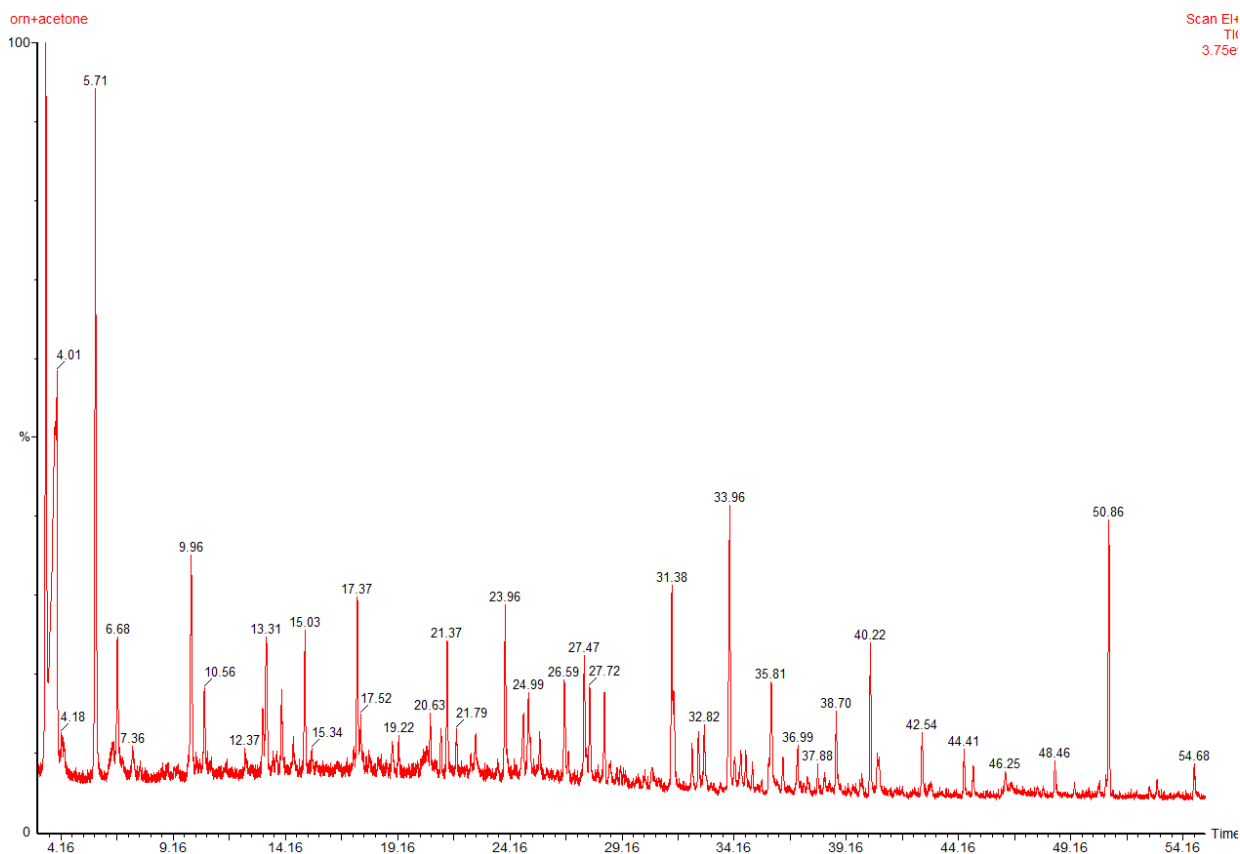


**Figure 4- 1** (a) Corn stover and (b) soybean straw ash content as seen under SEM and XRD

#### 4.3.1.1.GC-MS characterization of corn stover and soybean straw pyrolysis oils

Chemical characterization of two pyrolysis oils performed on GC/MS. (Figure 4-2 and Table 4-3) shows the chemical compounds in the crude corn stover pyrolysis oil. The compounds identified from soybean straw pyrolysis oil are listed in Figure 4-3 and Table 4-4. These are the same as reported for fast pyrolysis liquids and include carboxylic acids, alcohols, aldehydes, ketones, esters, hydrocarbons, furans, phenolic and aromatic compounds. Except water fraction,

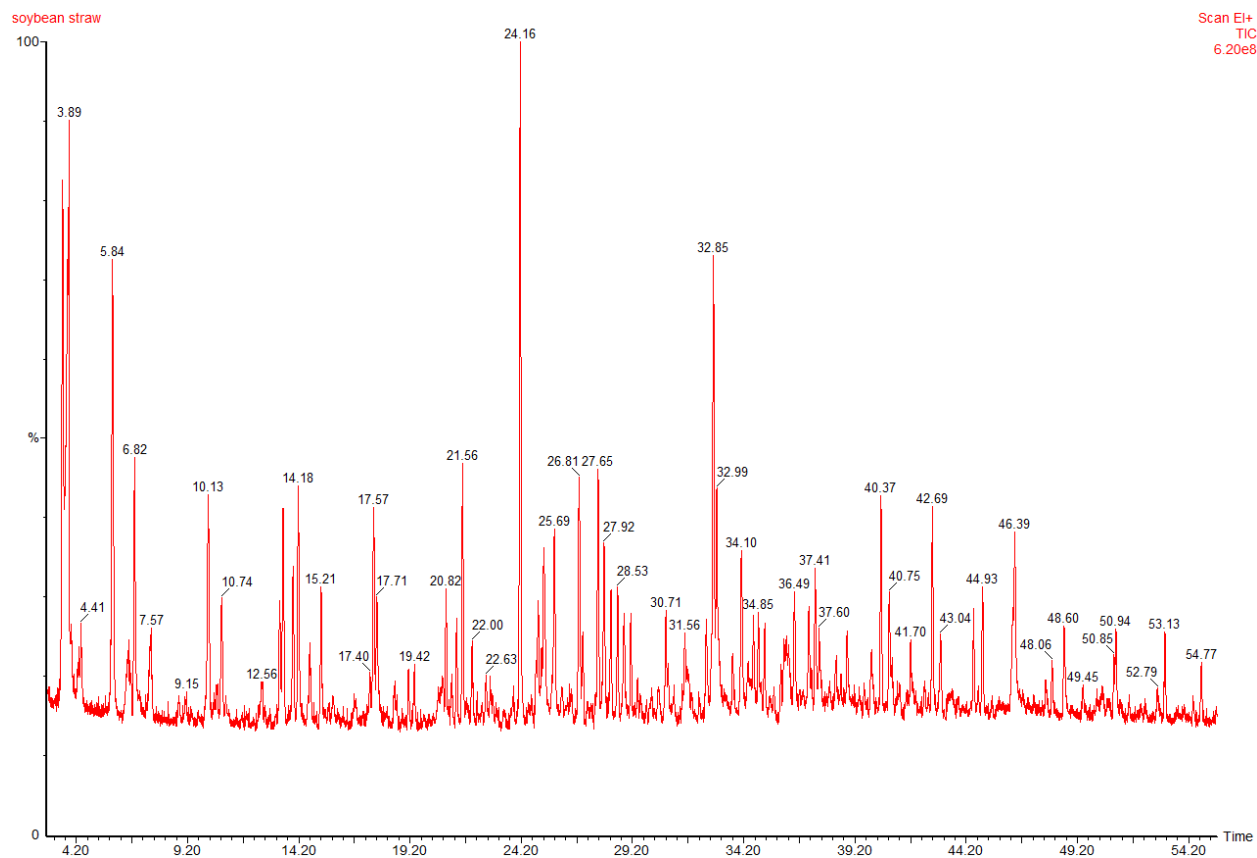
the compounds most abundant in the pyrolysis oils were water soluble oxygenated compounds derived from polysaccharide. The most abundant compounds in this class are levoglucosan, hydroxyacetaldehyde, acetol and acetic acid.[78] Phenolic compounds derived from lignin fraction also account for a large portion in both pyrolysis oil samples. The most abundant lignin-derived small molecule in the corn stover and soybean straw pyrolysis oil was phenol.[8, 79]



**Figure 4- 2** Total ion chromatogram of a corn stover-derived sample of pyrolysis oil

**Table 4- 3** GC/MS analysis of pyrolysis oil derived from corn stover

<b>ID.</b>	<b>Compound</b>	<b>Formula</b>	<b>Group</b>	<b>M<sub>w</sub></b>	<b>RT (min)</b>	<b>Area%</b>
1	hydroxyacetaldehyde	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	aldehyde	60	3.49	5.560
2	acetol	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	ketone	74	5.71	6.163
3	2-hydroxy-1-one-2-cyclopenten	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	ketone	98	13.15	0.708
4	2-butanone	C <sub>4</sub> H <sub>8</sub> O	ketone	72	14.51	0.340
5	acetoxyacetone	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	ketone	116	15.03	1.193
6	3-methyl-2-cyclopentenone	C <sub>6</sub> H <sub>8</sub> O	ketone	96	20.63	0.534
7	2-hydroxy-3-methyl-2-cyclopentene-1-one	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	ketone	112	23.96	1.656
8	guaiacyl acetone	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	ketone	180	47.92	0.100
9	acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acid	60	4.01	10.386
10	n-hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	acid	256	63.53	0.378
11	ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	alcohol	62	6.68	1.905
12	hexaethylene glycol	C <sub>12</sub> H <sub>16</sub> O <sub>7</sub>	alcohol	282	75.01	0.388
13	methyl acetate	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	ester	74	9.96	2.710
14	2-hydroxy-butyrolactone	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	ester	102	21.79	0.455
15	furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	furan	98	13.31	1.764
16	2(5H)-furanone	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	furan	84	17.37	1.832
17	5-methyl-5H-furan-2-one	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	furan	98	18.93	0.399
18	furan	C <sub>4</sub> H <sub>4</sub> O	furan	68	19.22	0.236
19	4-methyl-5H-furan-2-one	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	furan	98	21.11	0.439
20	phenol	C <sub>6</sub> H <sub>6</sub> O	phenol	94	21.37	1.326
21	<i>o</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	25.49	0.419
22	<i>p</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	26.59	1.207
23	guaiacol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	phenol	124	27.47	1.083
24	4-ethyl-phenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	31.38	1.796
25	2-methoxy-4-methyl phenol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	phenol	138	32.82	0.633
26	3-ethyl-5-methyl phenol	C <sub>9</sub> H <sub>12</sub> O	phenol	136	34.97	0.240
27	2-methoxy-4-ethyl phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	phenol	152	36.99	0.513
28	2-methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	phenol	150	38.70	0.783
29	syringol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	phenol	154	40.23	1.320
30	eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	phenol	164	40.61	0.321
31	vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	phenol	152	42.54	0.635
32	methyl syringol	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	phenol	168	44.41	0.471
33	acetoguaiacone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	phenol	166	46.25	0.332
34	4-propenyl syringol (cis)	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	phenol	194	52.68	0.107
35	syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	phenol	182	53.01	0.187
36	4-propenyl syringol (trans)	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	phenol	194	54.68	0.336
37	acetosyringone	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	phenol	196	55.69	0.219
38	2,3-dihydrobenzofuran	C <sub>8</sub> H <sub>8</sub> O	aromatic	120	33.96	2.915
39	4-hydroxy benzaldehyde	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	aromatic	122	40.54	0.387
40	1,2,3-trimethoxy-5-methylbenzene	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	aromatic	182	47.66	0.116
41	hexadecane	C <sub>16</sub> H <sub>34</sub>	alkene	226	50.86	2.507



**Figure 4- 3** Total ion chromatogram of a soybean straw-derived sample of pyrolysis oil

**Table 4- 4** GC/MS analysis of pyrolysis oil derived from soybean straw

ID	Compound	Formula	Group	M <sub>w</sub>	RT (min)	Area %
1	acetol	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	ketone	74	5.84	3.216
2	acetoxycetone	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	ketone	116	15.21	0.845
3	glycolaldehyde	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	aldehyde	60	3.58	3.632
4	propanal	C <sub>3</sub> H <sub>6</sub> O	aldehyde	58	10.73	0.809
5	nonalnal	C <sub>9</sub> H <sub>18</sub> O	aldehyde	142	28.53	0.725
6	acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acid	60	3.89	6.151
7	larixic acid	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	acid	126	28.82	0.732
8	ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	alcohol	62	6.82	1.575
9	diacetone alcohol	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	alcohol	116	13.94	0.941
10	ethyleneglycol monoacetate	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	alcohol	104	14.18	1.432
11	1,3-propanediol	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	alcohol	76	22.00	0.475
12	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	furan	96	13.49	1.388
13	2(5H)-furanone	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	furan	84	17.57	1.379
14	butyrolactone	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	furan	86	17.71	0.939
15	5-methyl-2(5H)-furanone	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	furan	98	19.13	0.354
16	furan	C <sub>4</sub> H <sub>4</sub> O	furan	68	19.62	0.399
17	phenol	C <sub>6</sub> H <sub>6</sub> O	phenol	94	21.56	1.325
18	<i>o</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	25.69	1.155
19	<i>p</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	phenol	108	26.81	1.666
20	guaiacol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	phenol	124	27.65	1.328
21	3-ethyl-2-hydroxy-2cyclopentenone	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	phenol	126	29.12	0.492
22	3,5-dimethylphenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	30.71	0.615
23	3-ethyl-phenol	C <sub>8</sub> H <sub>10</sub> O	phenol	122	31.56	0.586
24	catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	phenol	138	32.85	2.523
25	3-ethyl-5-methyl phenol	C <sub>9</sub> H <sub>12</sub> O	phenol	136	35.148	0.462
26	1,4-benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	phenol	110	36.49	0.792
27	2-methoxy-4-ethyl phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	phenol	152	37.14	0.658
28	4-methyl-1,2-benzenediol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	phenol	124	37.41	0.709
29	2-methoxy-4-vinylphenol	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	phenol	150	38.85	0.510
30	2-methyl-1,4-benzenediol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	phenol	124	39.94	0.549
31	syringol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	phenol	154	40.38	1.174
32	eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	phenol	164	40.76	0.729
33	vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	phenol	152	42.69	1.144
34	methyl syringol	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	phenol	168	44.53	0.521
35	isoeugenol (trans)	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	phenol	164	44.93	0.701
36	acetoguaiacone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	phenol	166	46.39	2.03
37	syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	phenol	182	53.13	0.493
38	4-propenylsyringol (trans)2-cyclopenten	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	phenol	194	54.77	0.356
39	1-one,2-hydroxy-3-methyl-cyclopenten	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	cyclic	112	24.16	3.856

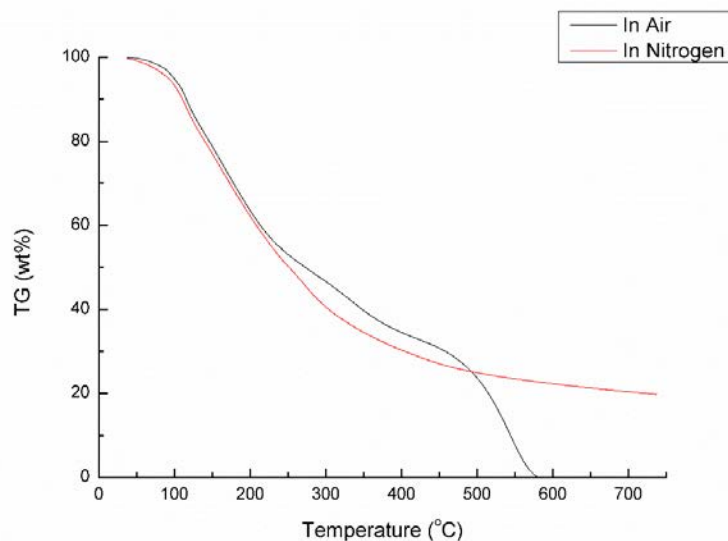
ID	Compound	Formula	Group	M <sub>w</sub>	RT (min)	Area %
40	cyclopentanol	C <sub>5</sub> H <sub>10</sub> O	cyclic	86	27.93	1.159
41	L-glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	sugar	180	28.24	0.743
42	1,4:3,6-dianhydro-glucofuranose	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	sugar	144	34.10	1.110
43	Lactose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	sugar	342	34.64	0.487
44	D-glucose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	sugar	342	48.06	0.337
45	hexadecane	C <sub>16</sub> H <sub>34</sub>	hydrocarbon	226	50.94	0.556
46	3(2H)-pyridazino	C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O	Nitric	96	21.08	0.327

A total of 46 chemical compounds identified by GC-MS correspond to about 55% of the total area. The remaining fraction was constituted by more than 200 compounds with less than 0.2 area% individually. According to the methods for chemical characterization developed for pyrolysis oils, the amount of liquid not included in the table is presumably the nonvolatile compounds and the water fraction.

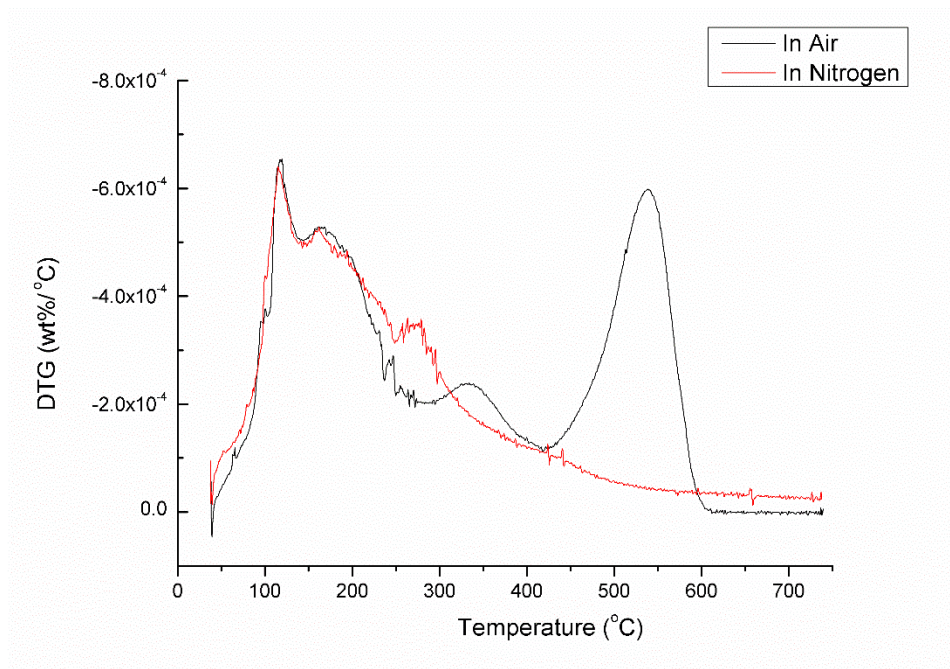
#### 4.3.1.2. Thermogravimetric analysis

The TGA in our study was used to characterize the thermal stability, evaporation and combustion properties of pyrolysis oils.

(a)



(b)



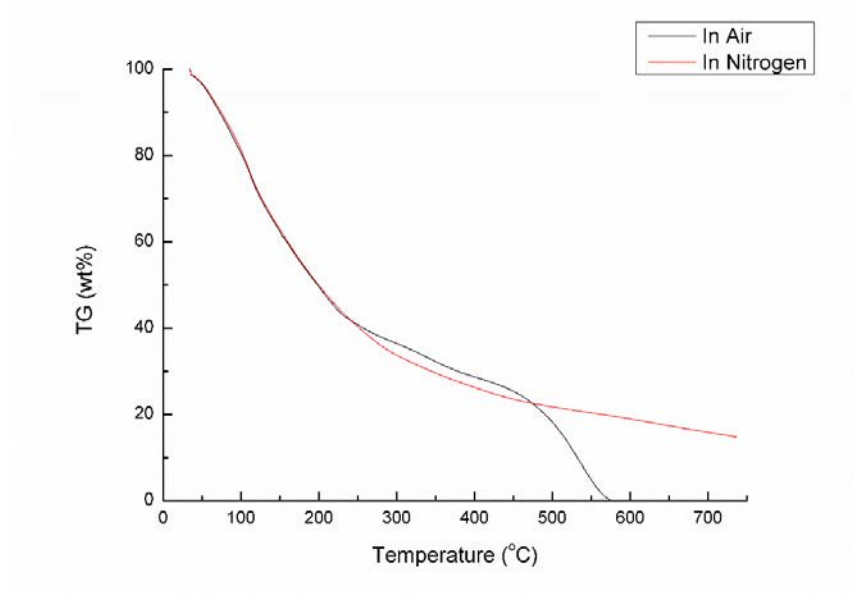
**Figure 4- 4** (a & b) TG and DTG curves of corn stover-derived pyrolysis oil heated in N<sub>2</sub> and air

Figure 4-4 (a) shows the TGA percent weight loss of corn stover-derived pyrolysis oil in a N<sub>2</sub> atmosphere or under an air atmosphere at heating rate of 10 °C/min from room temperature to 750°C. The TGA traces were analyzed using differential method to obtain the pyrolysis kinetic parameters from the thermogravimetric data as DTG data (Fig. 4-4 b). The DTG curves also help to define the beginning and the end of each event of mass loss.[80] The thermogravimetric behavior of the corn stover-derived pyrolysis oil showed similarities in nitrogen and air atmospheres before 421°C. From the DTG curves, two clear peaks at 114°C and 165°C were observed. At 114°C, the peak corresponds to the evaporation of water and low boiling points volatiles fraction in pyrolysis oil. After burning of this fraction, the weight loss was 21.2 wt%. The second peak at 165°C is attributed to the evaporation of another portion of volatiles with higher boiling points which could be acetic acid and aldehydes based on their boiling points range. Most mass loss occurred between 421°C to 600°C in air atmosphere where the DTG curve indicated the

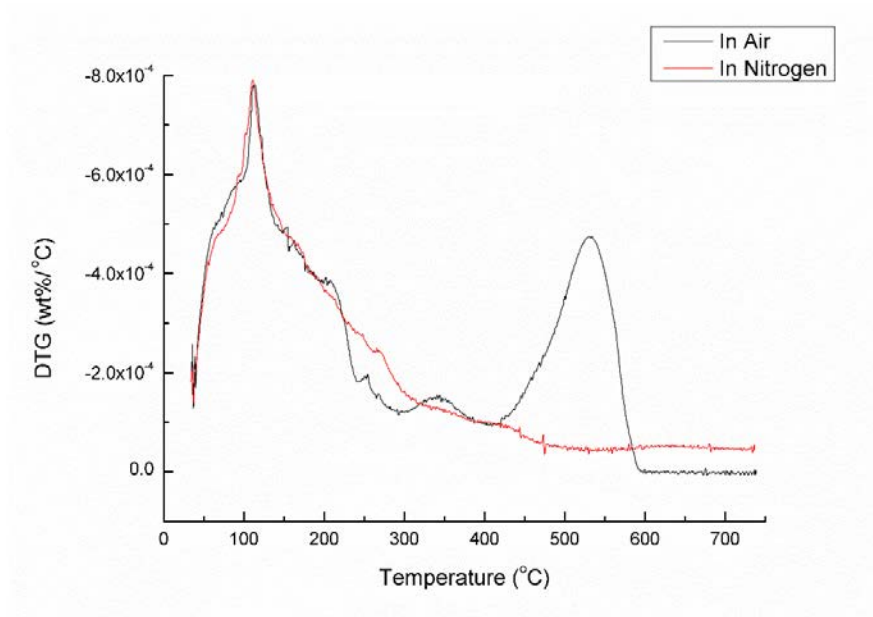


highest mass loss rate. No similar peak appeared in N<sub>2</sub> atmosphere, this is due to the fact that burning of char residues only occurred in air and all char content was burned off at 580°C where the total weight loss was 100%. The char yield of 32.9 wt% was attributed to the high inorganic materials in pyrolysis oil, which was characterized as ash content of feedstock.

(a)



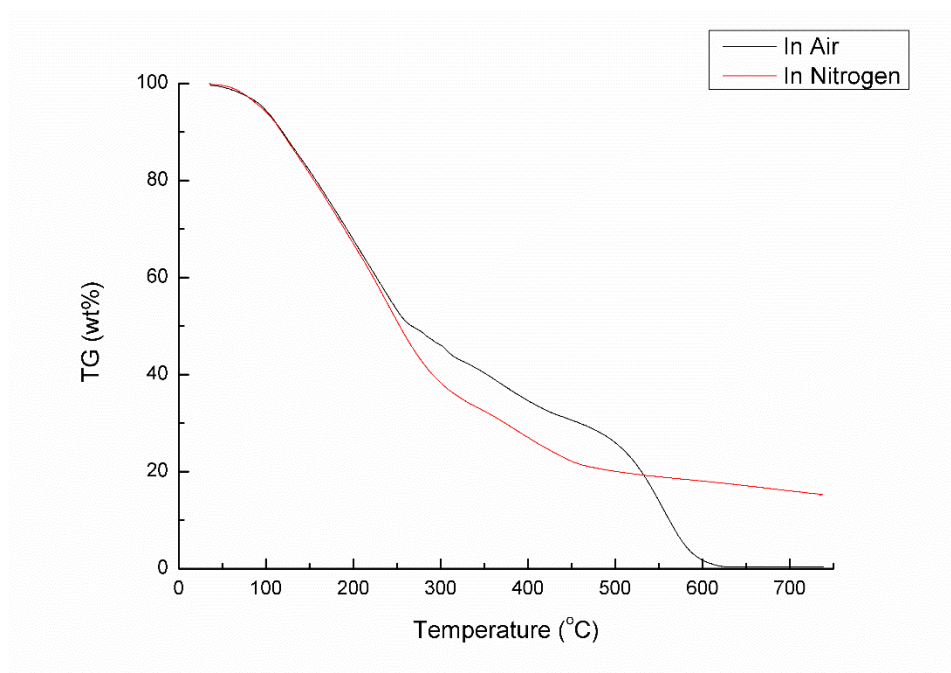
(b)



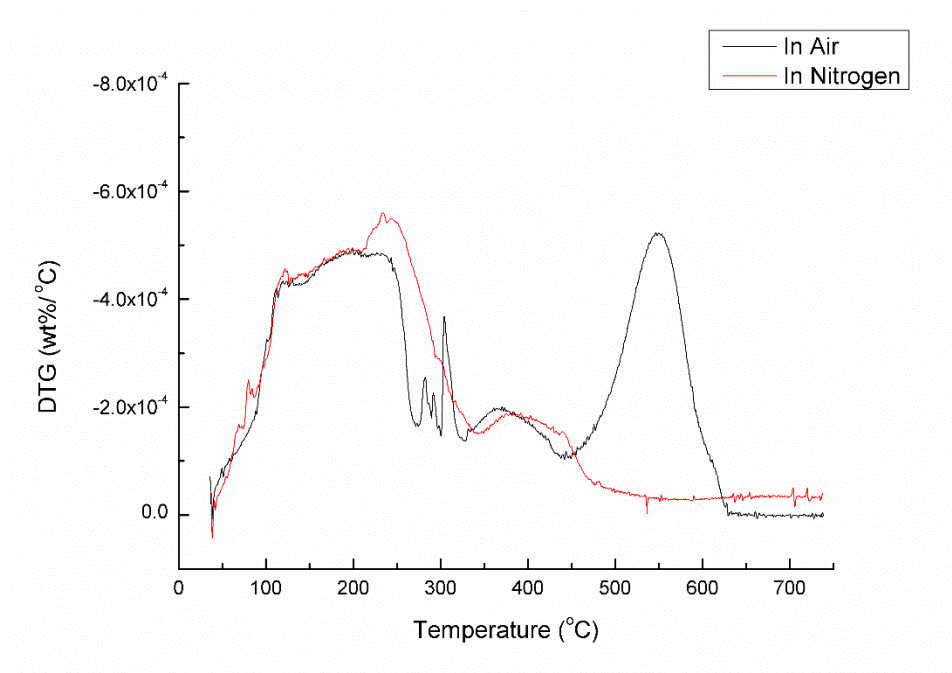
**Figure 4- 5** (a & b) TG and DTG curves of soybean straw-derived pyrolysis oil heated in N<sub>2</sub> and air

From the Figure 4-5 DTG graph of soybean straw pyrolysis oil, the first high weight loss occurred at 110 °C. The mass loss was 35.2 wt%. This loss was due to the evaporation of water and light volatile fraction. Comparing with corn stover-derived pyrolysis oil, soybean straw oil sample contained more low boiling points compounds fraction. Different than corn stover pyrolysis oil, from the DTG curve, there was no such similar peak found around 160°C, however, the largest weight loss in air atmosphere occurred at 400°C, which is same as corn stover pyrolysis oil. The char content in soybean straw was 27.8 wt%.

(a)



(b)



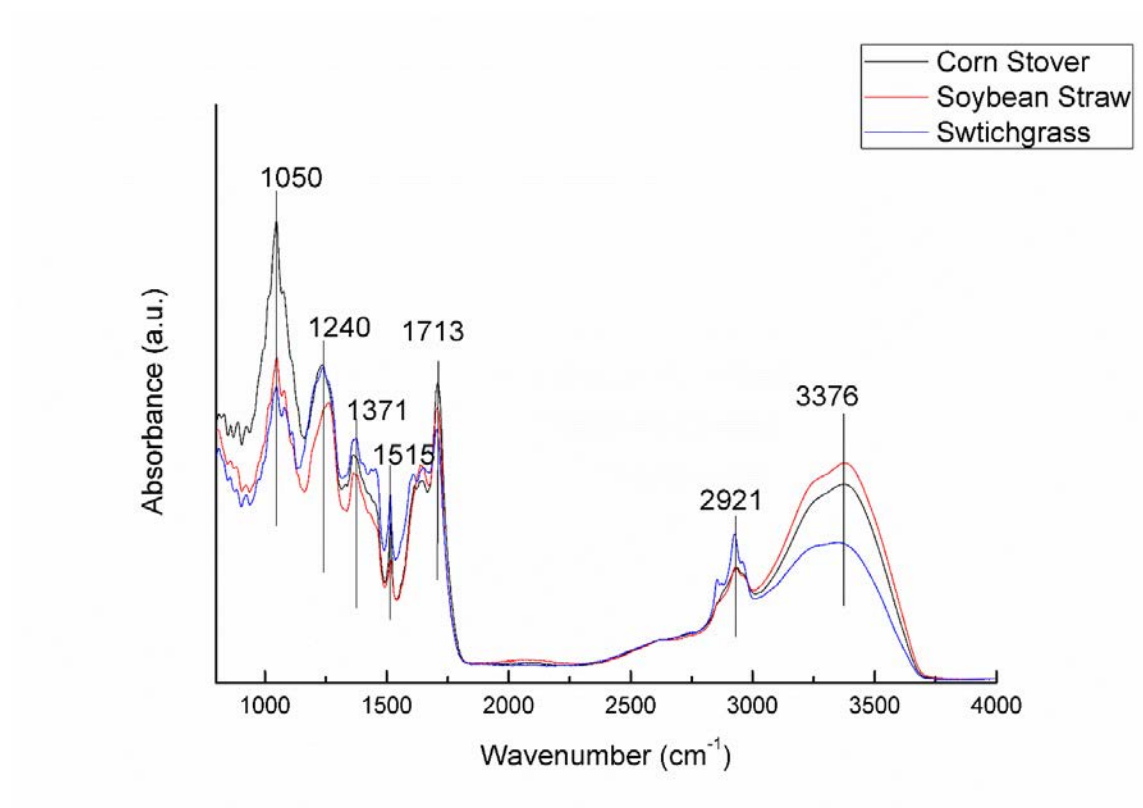
**Figure 4- 6** (a & b) TG and DTG curves of switchgrass-derived pyrolysis oil heated in N<sub>2</sub> and air

The DTG curves of switchgrass pyrolysis oil as shown in Fig 4-6 b, were very different from corn stover and soybean straw before 320°C. There are no clear peaks that represent weight loss of water and light volatiles at around 120°C, however when the temperature raises to between 260°C-320 °C, a few sharp peaks appeared at 282°C, 290°C and 303°C that indicate switchgrass pyrolysis oil may contain some heavy volatile fractions. The burning of char in switchgrass pyrolysis oil occurred at similar temperature range. Comparing with other two pyrolysis oil, it contained moderate percent of char, 30.9 wt%.

#### 4.3.1.3.FT-IR Data

The FT-IR spectra, representing the functional group of corn stover, soybean straw and switchgrass derived pyrolysis oils are shown in Fig. 4-7. The broad peak of the O-H stretching vibrations between 3200 and 3600 cm<sup>-1</sup> indicates the presence of water, alcohols and phenolics. The C=O stretching vibrations between 1705-1725 cm<sup>-1</sup> indicates the presence of ketones and

carboxylic acids. The presence of aromatics was indicated by the C-C stretching vibrations between 1510-1545  $\text{cm}^{-1}$  and the C-H bond deformation vibrations in aromatic rings at 1050  $\text{cm}^{-1}$ . The presence of alkane groups in the pyrolysis oil was indicated by the C-H stretching vibrations peak shown at 2850-3000  $\text{cm}^{-1}$ . In addition, the location of bending vibrations of C-H groups at 1371  $\text{cm}^{-1}$  provide another evidence for the presence of methyl groups in a given compound.[70] The above analysis is summarized in Table 4-5.



**Figure 4- 7** Comparison of FT-IR spectra of raw corn stover, soybean straw and switchgrass pyrolysis oils

In Fig. 4-7, soybean straw gave a highest O-H stretching vibrations and the FT-IR spectra of switchgrass pyrolysis oil showed the lowest concentration of O-H bonds vibrations, mainly consisted of water, alcohols and phenolics. This results show the soybean straw pyrolysis oil

contains higher concentration of –OH containing compounds. The functional group detected from pyrolysis oils are listed in Table 4-5.

**Table 4- 5** FT-IR functional group composition analysis of pyrolysis oil

<b>Wave number range (cm<sup>-1</sup>)</b>	<b>Peak wave number (cm<sup>-1</sup>)</b>	<b>Group</b>	<b>Compound</b>
3200-3600	3376	O-H stretching	Water, Alcohols
2850-3000	2921	C-H stretching	Alkanes
1705-1725	1713	C=O stretching	Carboxylic acids, Ketones
1510-1545	1515	C-C stretching	Aromatics
	1371	C-H bending	Methyl group in alkane
1030-1050	1240	C-O bending	Guaiacyl rings
	1050	C-H deformation	Aromatic

#### **4.3.2. Gas Analysis**

A total of 24 runs were completed and the data are listed in Table 4-6.

**Table 4- 6** Pyrolysis oil upgrading runs with corn stover-derived pyrolysis oil in a 300 mL batch reactor

Initial Conditions								Results				
Run	Catalysts (g)	Solvent (ml)	Oil (ml)	T (° C)	P <sub>i</sub> (psig)	P <sub>f</sub> (psig)	ΔP	pH <sub>i</sub>	pH <sub>f</sub>	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)
1	NiCl <sub>2</sub> (0.5)	PEG(25)	25	250	468	430	38	4.11	3.87	8.6	N/A	1
2	NiCl <sub>2</sub> (0.4)	PEG(20)	20	250	467	441	26	4.15	3.45	14.4	N/A	0.7
3	γ-Al <sub>2</sub> O <sub>3</sub> (1)	PEG(90)	10	250	201	206	-5	4.85	5.65	4.7	N/A	0
4	NiCl <sub>2</sub> (0.1)	PEG(90)	10	250	199	197	2	4.81	4.67	8.2	N/A	0
5	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	PEG(90)	10	270	206	197	9	4.81	4.63	7.52	N/A	0.4
6	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	PEG(90)	10	270	203	192	11	4.67	4.31	5.03	N/A	0
7	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	PEG(90)	10	230	207	205	2	4.83	4.43	1.88	93.8	0
8	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	PEG(90)	10	230	199	195	4	4.73	4.64	3.4	93.9	0
9	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	Hexadecane(90)	10	150	103	107	-4			3.1	95.2	0
10	γ-Al <sub>2</sub> O <sub>3</sub> (1) NiCl <sub>2</sub> (0.1)	Deionized Water(90)	10	80	103	101	2			0	98.2	0
11	γ-Al <sub>2</sub> O <sub>3</sub> (1) CoCl <sub>2</sub> (0.1)	PEG(90)	10	250	203	205	-2	4.79	4.96	6.7	92.7	0
12	Ru(bipy)(CO) <sub>2</sub> Cl <sub>2</sub> (0.5)	PEG(90)	10	150	213	157	56	4.85	3.39	0	97.7	0
13	Ru(bipy)(CO) <sub>2</sub> Cl <sub>2</sub> (0.5)	Hexadecane(90)	10	150	203	142	61			0	96.6	0
14	Ru/Al <sub>2</sub> O <sub>3</sub> (0.1)Ru 5 wt%	Hexadecane(90)	10	150	209	220	-11			9.5	85.4	0
15	Rh/Al <sub>2</sub> O <sub>3</sub> (0.5), Rh 5 wt%	PEG(90)	10	200	206	178	28	4.76	6.53	3.7	94.7	0

Initial Conditions								Results				
Run	Catalysts (g)	Solvent (ml)	Oil (ml)	T (° C)	P <sub>i</sub> (psig)	P <sub>f</sub> (psig)	ΔP	pH <sub>i</sub>	pH <sub>f</sub>	CO <sub>2</sub> (%)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)
16	Rh/Al <sub>2</sub> O <sub>3</sub> (0.5), Rh 5 wt%	PEG(90)	10	150	203	188	15	4.8	4.81	0	96.7	0
17	Ru/C (0.5), Ru 5 wt%	PEG(90)	10	150	197	188	9	4.75	4.67	2.1	97.7	0
18	Ru/C (0.5), Ru 5 wt%	PEG(90)	10	200	193	138	55	4.84	6.03	5.8	91.8	0
19	Rh/C (0.5), Rh 5 wt%	PEG(90)	10	200	187	151	36	4.81	6.13	4.2	94.2	0
20	Rh/C (0.5), Rh 5 wt%	PEG(90)	10	150	203	182	21	4.74	5.17	1.5	96.3	0
21	Ru/C (0.5), Ru 5 wt%	PEG(90)	10	200	197	150	47	4.75	4.86	2.5	96.5	0
22	Ru/C (0.5), Ru 5 wt%	PEG(90)	10	200	205	157	48	4.82	4.65	3.1	95.3	0
23	Ru(bipy)(CO) <sub>2</sub> Cl <sub>2</sub> (0.5)	PEG(90)	10	150	205	141	64	4.85	4.34	2.7	95.5	0
24	Ru/C (0.5), Ru 5 wt%	PEG(60)	0	200	203	199	4			0	99.2	0

PEG: Polyethylene glycol-400. P<sub>i</sub>=Initial pressure at 25°C, P<sub>f</sub>= Final pressure at 25 °C

The batch data in Table 4-6 show that:

1. The generation of CO<sub>2</sub> up to 14.4% on Run #2 suggests that O has been removed from the pyrolysis oil after catalytic treatment.
2. At first, it appears that the pH drop was not significant. But the generated CO<sub>2</sub> remains in solution in the batch mode and will increase the pH of the final solution.
3. A decrease in H<sub>2</sub> pressure is indicative of hydrogenation of pyrolysis oils. The Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/C and Ru(bipy)(CO)<sub>2</sub>(Cl)<sub>2</sub> catalysts show the effect on H<sub>2</sub> consumption at 150-200°C, which is relatively lower temperature compared to those reported in literature (350-400°C). Several tests showed these experiments are reproducible.
4. Different runs show that, under 230°C, no methane was found in the sample gases. This was a very desirable result for pyrolysis oil upgrading.
5. The results of Run #24 show that polyethylene glycol-400(PEG) solvent, with Ru/C catalyst retained its integrity after experiment.

Three different solvents were tried to dilute pyrolysis oil in order to decrease the viscosity. Water is very cheap and it helps to reduce the viscosity of pyrolysis oil. Moreover, low molecular weight alcohols are soluble in water. So the premise is that as alcohols form during reaction, they would go into the water phase that makes the separation of alcohol easy. Hexadecane was chosen as solvent because of its low vapor pressure. As an alkane solvent, hexadecane not only decreases the viscosity of pyrolysis oil but also increase the solubility of H<sub>2</sub>. Poly ethylene glycol (PEG) is miscible with pyrolysis oil. After stirring the mixture of pyrolysis oil and PEG-400, the two liquid phases became a uniform solution. This process greatly decreased the viscosity of pyrolysis oil.

As mentioned in Chapter 3, both chemical and physical properties of pyrolysis oils may vary for different feedstocks. Thus a few batch runs were completed using Ru/C and Rh/C in soybean



straw pyrolysis oil in order to examine their activity and selectivity on a different feedstock pyrolysis oil. A control group was done at 280°C, 1000 psig without catalyst. The results are listed in Table 4-7.

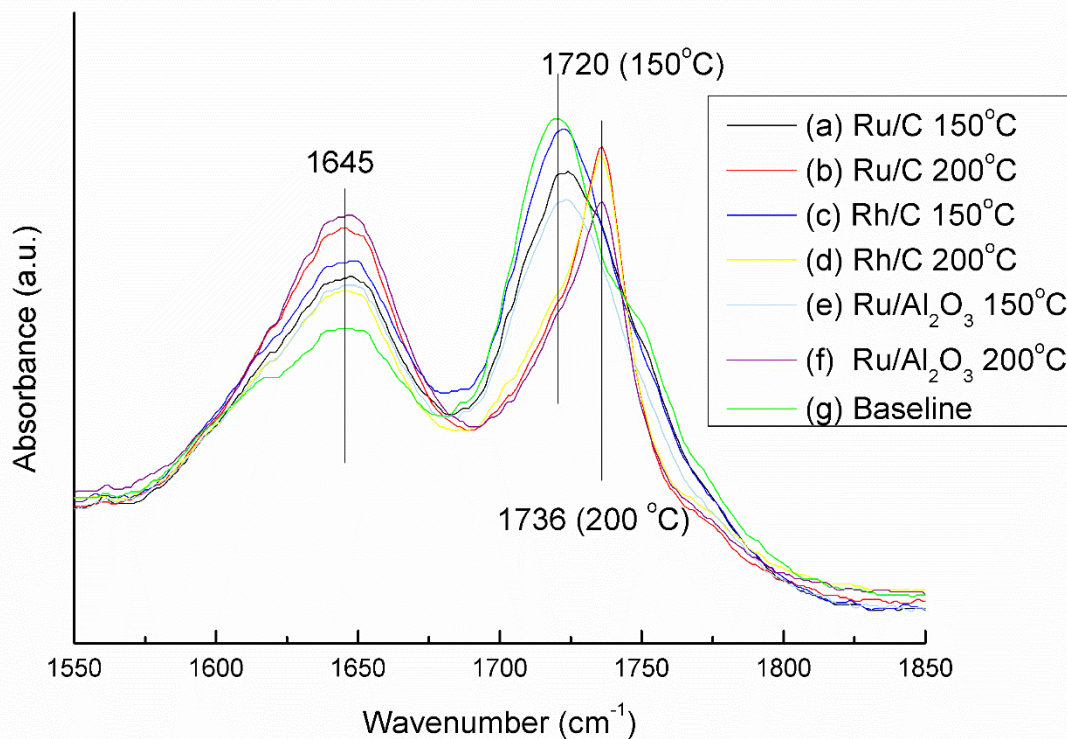
**Table 4- 7** Pyrolysis oil upgrading runs with soybean straw-derived pyrolysis oil in a 300 mL batch reactor

<b>Catalysts</b>	<b>Solvent (ml)</b>	<b>Oil (ml)</b>	<b>T (°C)</b>	<b>Pi (psig)</b>	<b>Pf (psig)</b>	<b>ΔP (psig)</b>	<b>CO (%)</b>	<b>CO<sub>2</sub> (%)</b>	<b>H<sub>2</sub> (%)</b>	<b>CH<sub>4</sub> (%)</b>
Ru/C	PEG(90)	10	280	989	868	121	0.28	1.10	87.4	0.11
Ru/C	PEG(80)	20	280	979	768	211	0.42	2.64	81.2	0.21
Rh/C	PEG(90)	10	280	972	857	115	0.35	0.76	89.8	0.09
No catalyst (baseline)	PEG(90)	10	280	969	962	7	0	0.21	92.33	0.10

The batch data in table 4-7 show that:

1. Both Ru/C and Rh/C gives high hydrogen consumption at 280 °C. Pressure drop were 121psig and 115psig respectively.
2. CH<sub>4</sub> was produced in small amount, below 0.21 %.
3. As the concentration of raw pyrolysis oil was doubled from 10 wt% to 20 wt%, both H<sub>2</sub> consumption and gas products concentration were doubled. This result suggests that the overall reactions occurring during HDO could be first order.
4. The baseline batch data shows extremely low pressure drop (7 psig) compared with catalyst presence. This pressure drop was assumed to be due to hydrogen solubility in the slurry under higher pressure during the reaction.

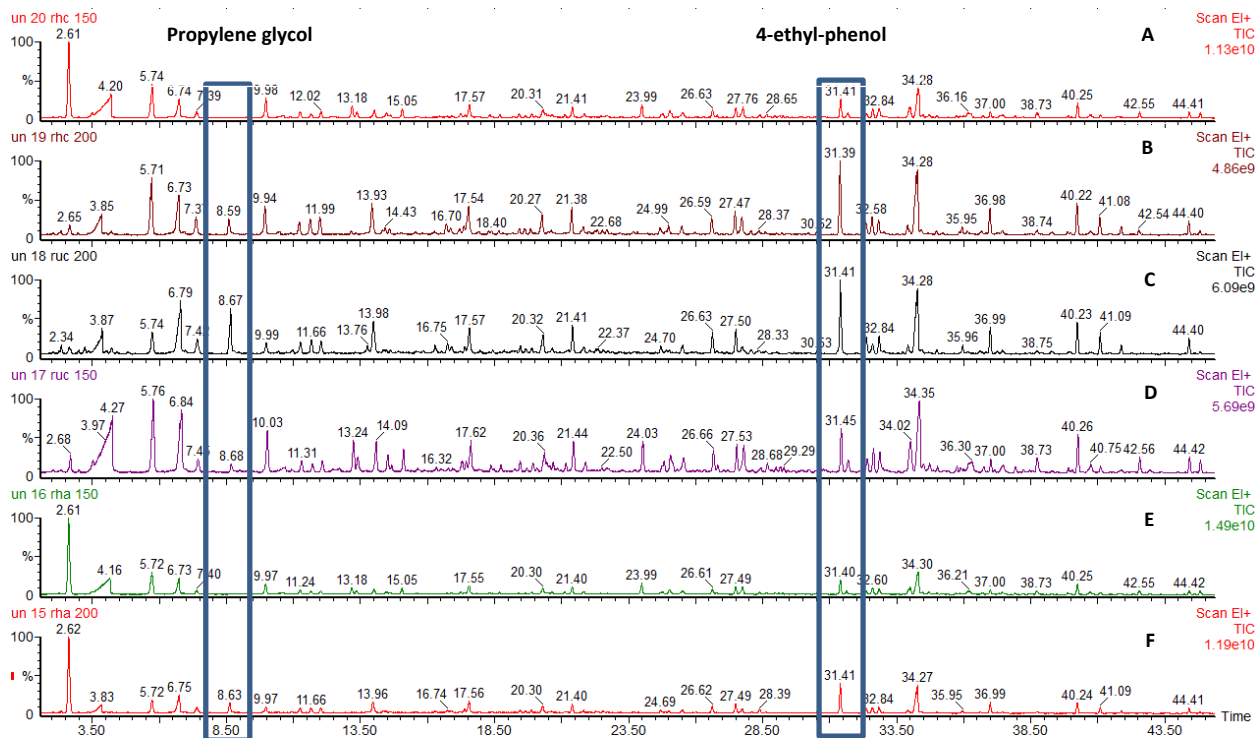
### 4.3.2.1.Liquid Analysis



**Figure 4- 8** Comparison of FT-IR spectra of HDO upgraded corn stover, soybean straw and switchgrass pyrolysis oils

Figure 4-8 shows the comparison of the FT-IR spectra of upgraded corn stover-derived pyrolysis oil over Ru/C, Rh/C and Ru/Al<sub>2</sub>O<sub>3</sub> at 150°C and 200°C. The baseline FT-IR spectrum of untreated pyrolysis oil diluted with solvent (PEG-400) shows the highest-intensity peak at 1720 cm<sup>-1</sup>. This peak represents the C=O bond vibrations from carboxylic acids group in pyrolysis oil and its intensity decreases as temperature increases from 150°C to 200°C. At 200°C, the majority of C=O from carboxylic acids were removed as CO<sub>2</sub>. A new peak appears at 1736 cm<sup>-1</sup> and this peak is only found when the temperature gets to 200°C and the appearance of this peak indicates the presence of C=O in ester group as the result of esterification. The peaks at 1645 cm<sup>-1</sup> represent the C=C stretching vibrations of alkenes. From Figure 4-8, Ru/C, Rh/C and Rh/Al<sub>2</sub>O<sub>3</sub> show good

selectivity towards producing hydrocarbons and alcohols. Ru/Al<sub>2</sub>O<sub>3</sub> also exhibited good activity for HDO and it has high surface area and activity due to Lewis acid sites; however many studies reported about its poor tolerance to water as it could turn to boemite (AlO(OH)) in the presence of water that would cause catalysts deactivation.[51] So, alumina is not a suitable support catalyst for pyrolysis oils upgrading as pyrolysis contains water fraction.



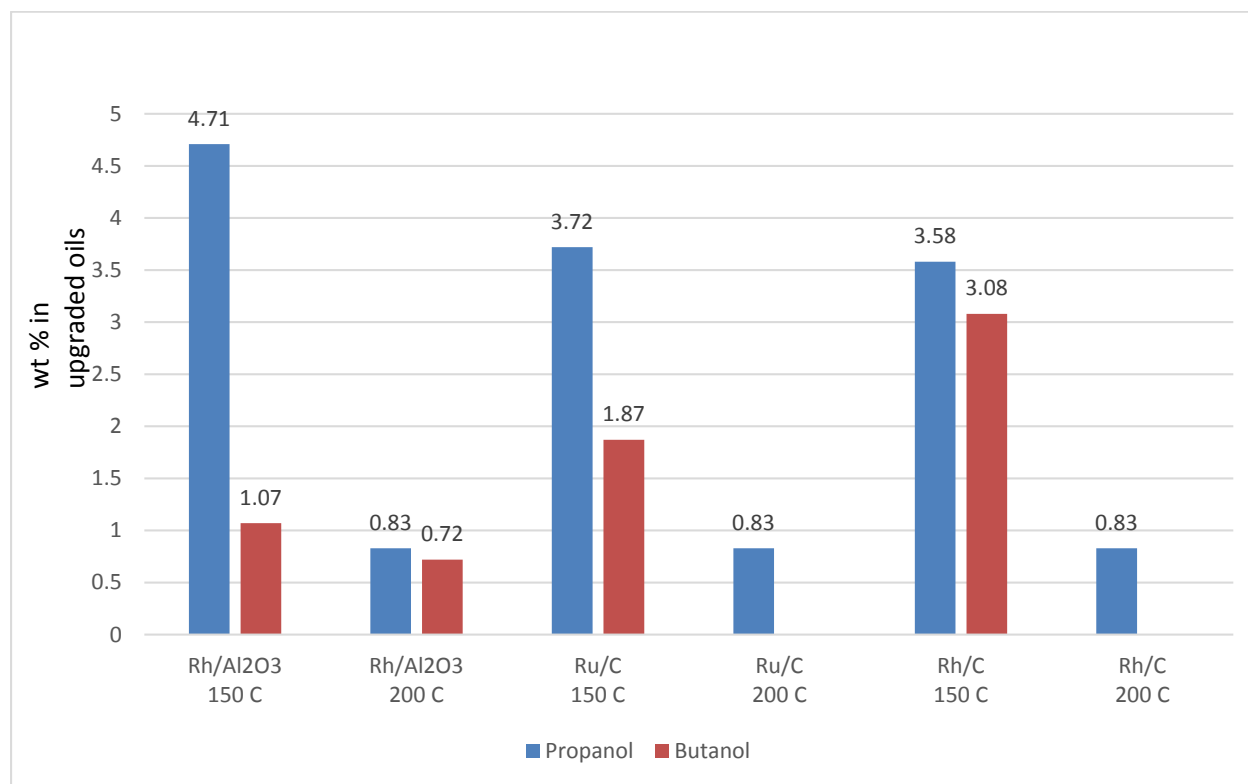
**Figure 4- 9** GC/MS data of multiple runs at different experimental conditions (a) Ru/C, 150°C, 200 psi (b) Rh/C, 200°C, 200 psi (c) Ru/C, 200°C, 200 psi (d) Ru/C, 150°C, 200 psi (e) Ru/Al<sub>2</sub>O<sub>3</sub>, 150°C, 200 psi (f) Ru/Al<sub>2</sub>O<sub>3</sub>, 150°C, 200 psi

**Table 4- 8** Individual compounds of selected components classed in upgraded corn stover pyrolysis oil produced using Ru/C, Rh/C and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts during the HDO reaction

Compound	Group	Relative area percentage (%)		
		Rh/C 200°C	Ru/C 200°C	Rh/Al <sub>2</sub> O <sub>3</sub> 200°C
Phenol	phenolics	2.895	2.781	2.113
2-methyl phenol	phenolics	1.056	1.117	1.046
4-ethyl phenol	phenolics	7.008	7.604	6.174
p-cresol	phenolics	1.930	2.293	1.685
2-methoxy phenol	phenolics	2.268	2.500	1.895
2,4-dimethyl phenol	phenolics	0.555	0.405	0.319
2-methoxy-4-propyl phenol	phenolics	9.427	10.687	8.692
cyclohexanone	cyclic compounds	4.154	4.333	3.262
cyclopentanone	cyclic compounds	1.577	1.539	1.428
4-ethyl cyclohexanone	cyclic compounds	0.372	0.331	0.205
ethylene glycol	alcohols	2.132	10.00	6.376
propylene glycol	alcohols	-	5.641	2.742
2-dodecanol	alcohols	0.316	0.295	0.178
Acetic acid ethenyl ester	ester	0.350	0.249	0.214
2,4-hexadienedioic acid,3,4-dithyl-,dimethyl ester	ester	18.207	20.564	19.425

The Rh/C, Ru/C and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts were chosen to investigate their selectivity for valuable products as they showed relatively high hydrogen consumption at 200 °C. Figure 4-9 shows propylene glycol and 4-ethyl-phenol products traces in GC/MS data. Table 4-8 shows the individual compounds of selected component identified by GC/MS. The majority of products are still oxygenated compounds after upgrading. Among them, phenolics account for up to 27 area%, cyclic compounds account for 6 area%, up to 16 area% of alcohols and 20 area% of esters. These results correspond to the FT-IR data as C=O vibration presented in upgraded pyrolysis oils. The oxygenates were produced when the reaction temperature was as low as 200°C, leading to low

deoxygenation activity. However, at lower temperatures, ketones and aldehydes were easier to form alcohols by C=O hydrogenation rather than further produce alkanes from C-O cleavage by hydrogenolysis, which requires higher dissociation energy.

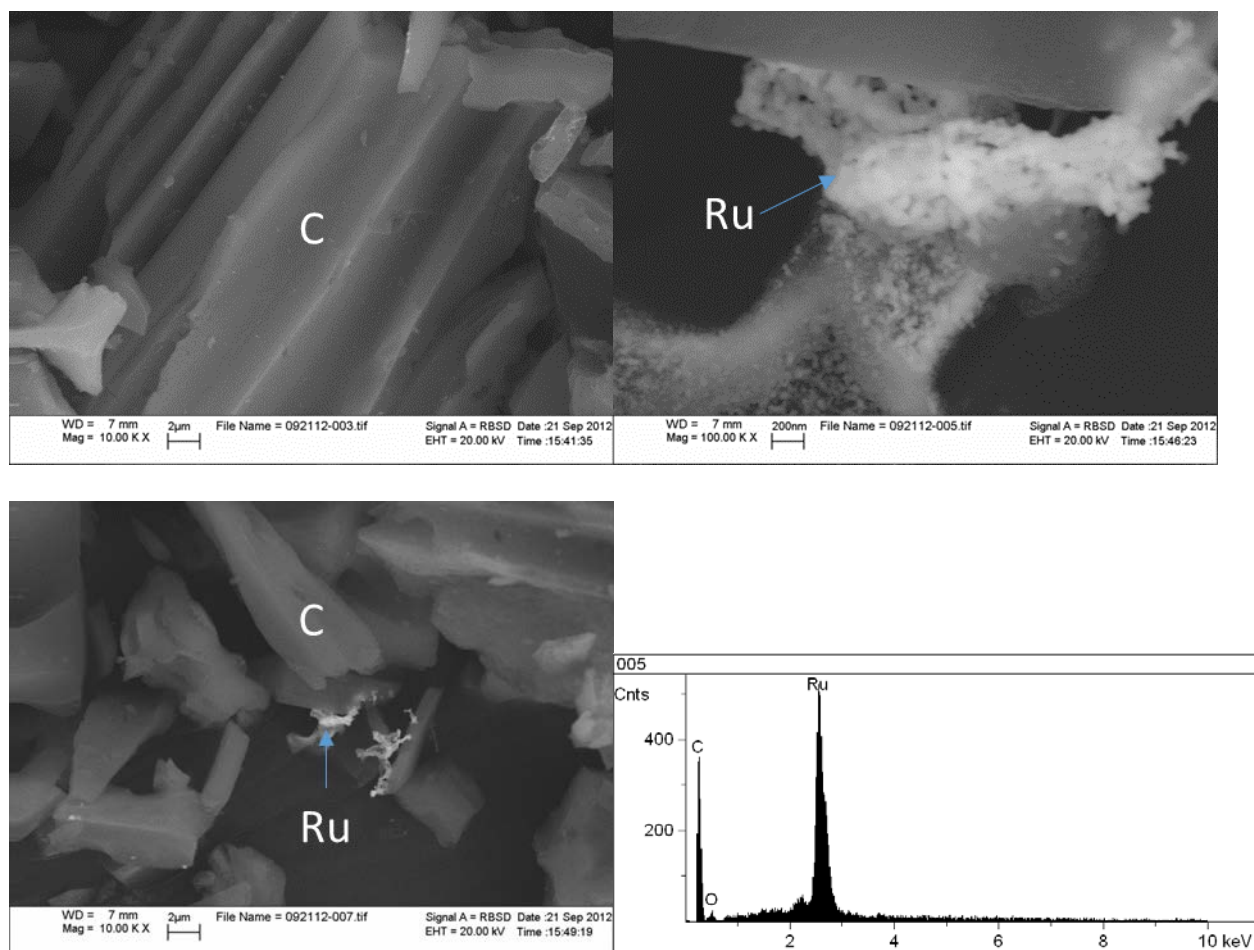


**Figure 4- 10** GC quantitative analysis of alcohol products in upgraded corn stover-derived pyrolysis oil

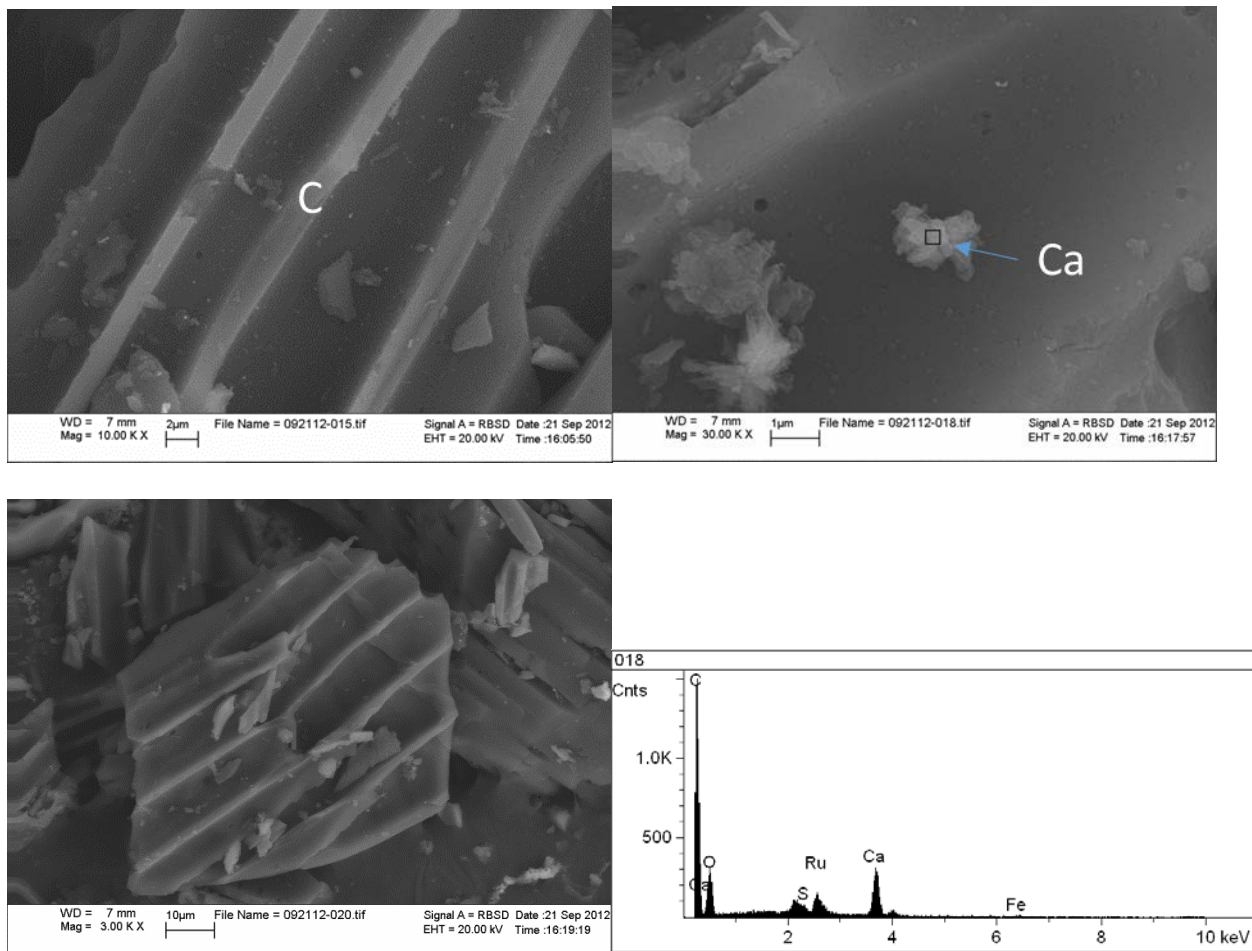
Alcohols produced from HDO of corn stover-derived pyrolysis oil were quantitatively measured by GC. A mixture of C<sub>1</sub>-C<sub>10</sub> straight-chain alcohols were used as the reference sample. The major alcohols found in upgraded pyrolysis oils were propanol and butanol as shown in Figure. 4-10. The proposed reaction path for straight-chain alcohols formation is via two main pathways: 1) The de-esterification yielded alcohols 2) hydrogenation of C=O of aldehyde to produce alcohols.[81] Other than straight-chain structure alcohols, alcohols such as branched alcohols and diatomic alcohol were also observed from the GC/MS data but with small area%. The products weight concentration maximized at 150 °C with all three catalysts used. The highest propanol

concentration obtained was 4.71 using Rh/Al<sub>2</sub>O<sub>3</sub> at 150°C. For butanol, a maximum concentration (3.08 wt %) was produced using Rh/C at 150°C. However, as the temperature was raised to 200°C, the concentration of two alcohols were below 1 wt%. This is because at lower temperatures, aldehydes and ketones to form alcohols via hydrogenation is favored. Moreover, at higher temperatures, alcohols start undergoing secondary reactions. A large amount of them react with carboxylic acid to produce ester as shown in the FT-IR data in figure 4-8. Another portion of alcohols is lost to gas phase (mostly methane and ethane) at 200°C. For the process to be economically attractive, this carbon loss needs to be minimized.

### 4.3.3. SEM image and XRD spectrum of catalysts

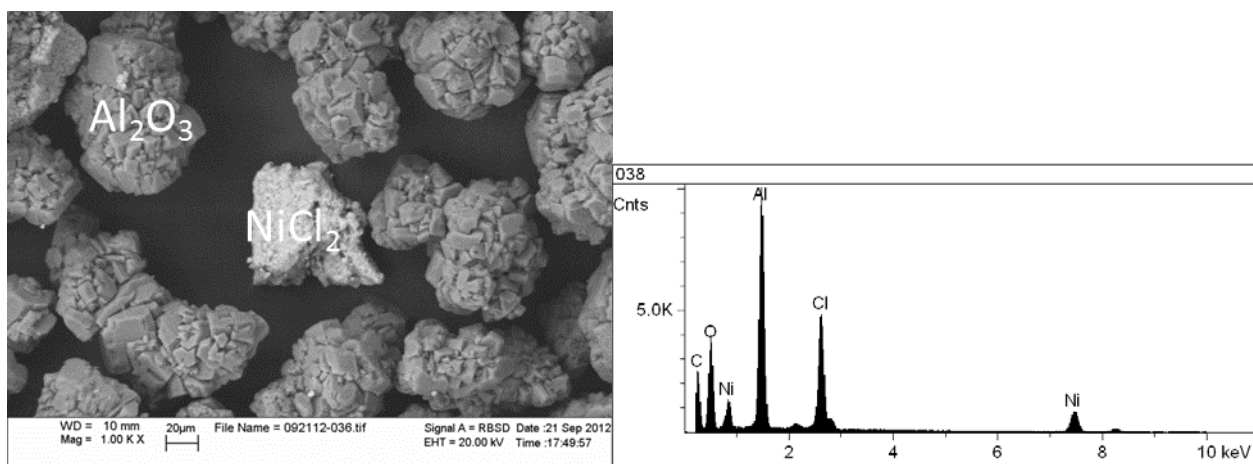
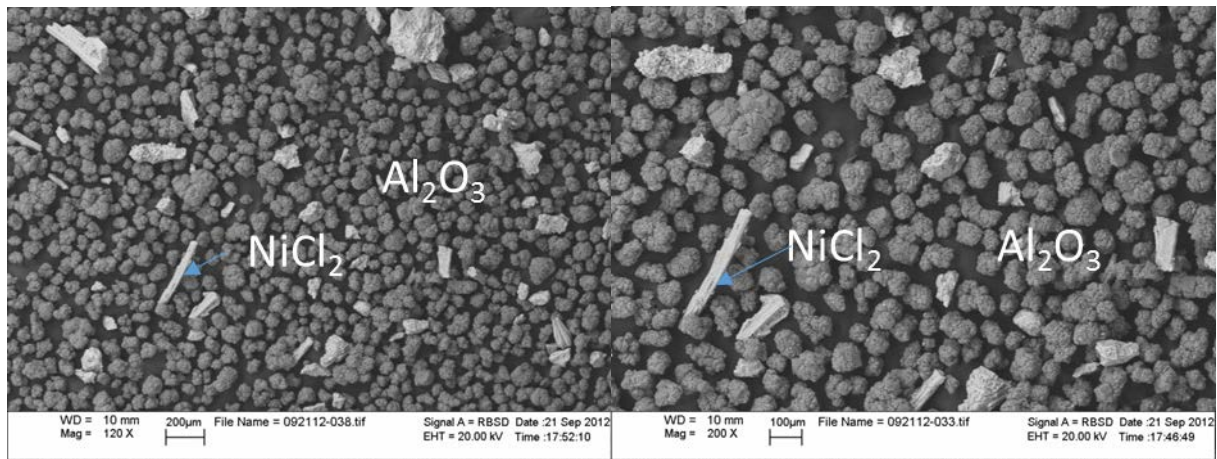


**Figure 4- 11** SEM Images and XRD spectrum of fresh Ru/C (5 wt%)

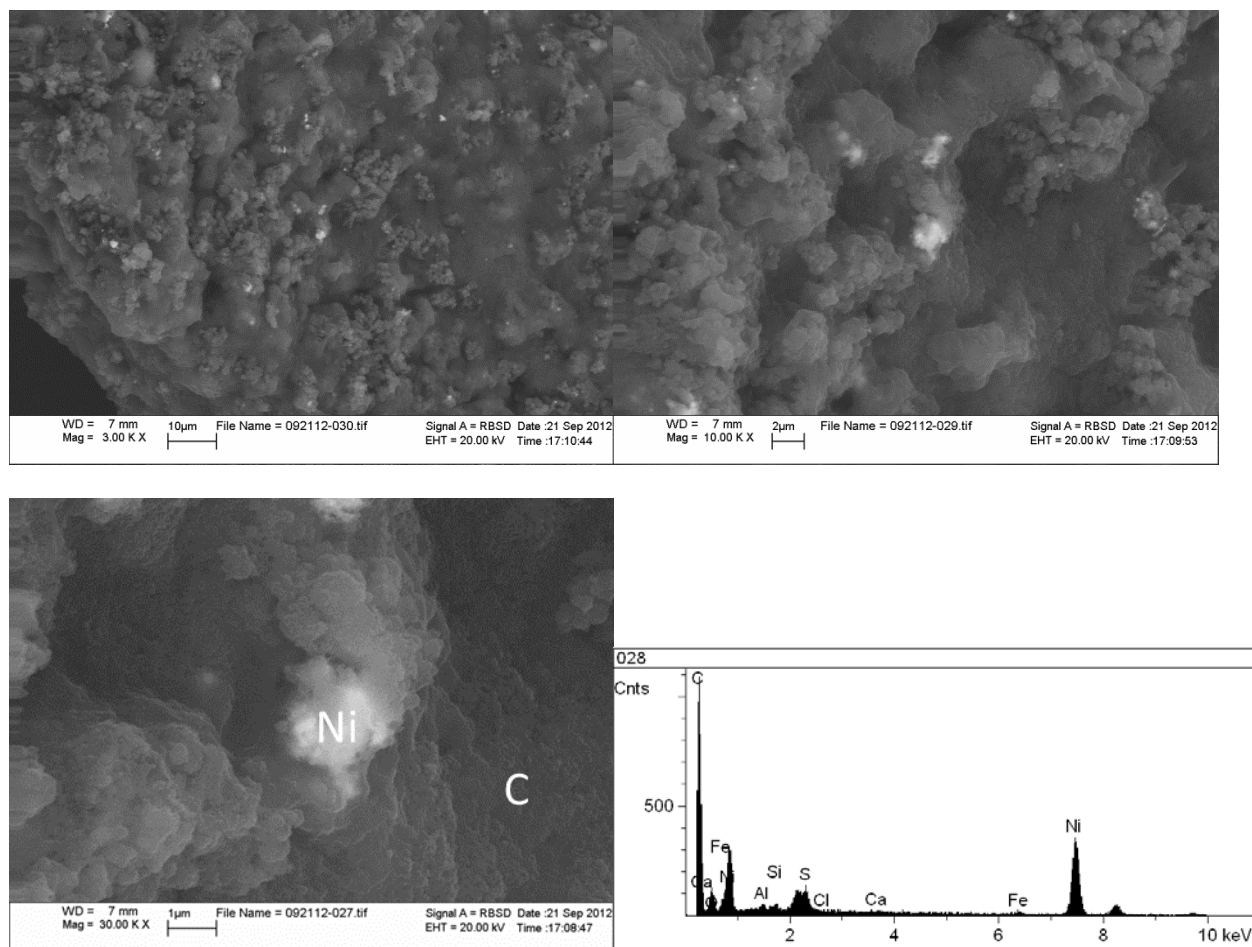


**Figure 4- 12** SEM Images and XRD spectrum of Ru/C after HDO reaction (200°C 190 psig)





**Figure 4- 13** SEM Images and XRD spectrum of fresh NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>



**Figure 4- 14** SEM Images and XRD spectrum of  $\text{NiCl}_2/\text{Al}_2\text{O}_3$  after HDO reaction  
(200°C, 197 psig)

The used catalysts were washed with acetone, filtered and then dried in the oven at 60°C for 2 hours. Calcination was not applied in this study in order to maintain the surface morphology of used catalysts. Fig. 4-11 shows the SEM images and the EDAX spectra of fresh Ru/C. It can be seen that the catalyst was flake shaped and crushed into smaller size. Ru particles were dispersed on the fractured area of carbon. The SEM images of used Ru/C are shown in Fig.4-12. The impurities such as Ca, K, and Fe were found as residue on the surface of carbon substrate. These impurities were from ash content of raw pyrolysis oil, other than impurities, Ru/C maintained its

catalyst surface morphology after 5 hours high temperature and high pressure reaction and this makes regeneration of Ru/C feasible.

NiCl<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were precursor catalysts and used after physically mixing. After the HDO reaction, the SEM image in Figure 4-14 shows NiCl<sub>2</sub> was reduced to Ni in H<sub>2</sub> atmosphere. So, unlike Ru/C and Rh/C, NiCl<sub>2</sub> is reduced catalyst. However, Ni was found to be coated by char after HDO that resulting in catalyst deactivation. Moreover,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was not found in the EDAX data. This is because  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> transformed to boemite (AlO(OH)) in the presence of water. This result further showed that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is not a promising supportive catalyst in pyrolysis oil upgrading process.

#### **4.4. Conclusion**

Pyrolysis oil samples have about 50% of oxygen that is associated with more than 300 oxygenated compounds. The majority of those compounds are phenolics and sugars and water. In order to remove oxygen and increase its heating value, hydrotreating of pyrolysis oils over numerous catalysts were studied. The Ru/C, Rh/C and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts were effective for further reducing the oxygen content based on the high hydrogen consumption. The composition of the upgraded products was studied by GC, GC/MS and FT-IR. Compositionally, the upgraded products from hydrotreating were 27% phenolics, 6% cyclic compounds, 16% alcohols and 20% of esters. The FT-IR data confirmed the increased ester C=O intensity and decreased carboxylic acid C=O intensity as the temperature increased from 150 °C to 200 °C. A higher concentration of alcohol products were found at a lower operating temperature. These results demonstrated the possibility of alcohol generation from HDO of pyrolysis oil under mild conditions.

## **Chapter 5. Conclusions and Future Work**

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## 5.1. Conclusions

The energy crisis and environmental concerns are prompting researchers and policy makers to seeking biomass-based sustainable energy solutions. Liquid fuel derived from biomass pyrolysis is a feasible option, however, the high oxygen content of pyrolysis oil that induces self-polymerization is a challenge for its storage and application as a transportation fuel. Therefore, oxygen content must be reduced to achieve energy content and properties similar to petroleum fuels. HDO is very promising and effective way of upgrading pyrolysis oil into transportation fuels. But self-polymerization during HDO promotes coke and char formation that leads to catalyst deactivation. Moreover, a low-cost HDO process is highly desirable.

To make HDO process of pyrolysis oil more economical, we attempted several approaches. Specific to this study, supported catalysts were chosen to enhance catalyst activity and decrease catalyst loading. Catalysts such as Ru, Rh (5 wt% loading on a support) were used as catalysts. The supports also helped maintain catalyst dispersion. A temperature of  $< 300^{\circ}\text{C}$  was selected to reduce the reactivity of pyrolysis oil, thereby minimizing self-polymerization. In addition to that, when temperature was  $< 250^{\circ}\text{C}$ , the production of  $\text{CH}_4$ , which is an unwanted product, could be minimized. As the majority ( $> 90\%$ ) of exhaust gas was  $\text{H}_2$ , HDO was in hydrogen-excess mode during HDO. Thus, the initial  $\text{H}_2$  pressure was kept below 1000 psig.

PEG is a good solvent to dilute pyrolysis oil because it is fully miscible with pyrolysis oil and maintains its integrity during the HDO reaction. By adding high ratio of PEG, the viscosity of pyrolysis oil was decreased. Combined with the mild reaction conditions, self-polymerization was restrained to 0.2 wt% of solid as collected after HDO. The SEM images of the catalysts were found to exhibit similar morphology before and after HDO treatment and a total of over 3600 cycles of

hydrogen activation in Ru showed that the system was catalytic in Ru and it remained active during HDO processing.

Of the various supported catalysts evaluated, Ru/C (5 wt%) and Rh/C (5 wt%) were successfully demonstrated as efficient catalysts for HDO of pyrolysis oil based on H<sub>2</sub> consumption (up to 257NL/kg of pyrolysis oil) and production of CO<sub>2</sub> (up to 19NL/kg of pyrolysis oil). The main products in upgraded pyrolysis oil included alcohols, cyclic compounds, hydrocarbons and phenolics. From the results obtained in this study, higher temperatures and pressures tend to produce hydrocarbons and mild condition favors alcohols generation because aldehydes and ketones readily react with H<sub>2</sub> to form alcohols under mild conditions rather than further hydrogenolysis of C-O to produce hydrocarbons. The amount of alcohols produced was also affected by aldehydes and ketones portion in feedstock as seen by GC/MS analysis. The acids in pyrolysis oils were fully removed after HDO at 280°C. The operating pressure plays an important role to keep water in liquid state and improve H<sub>2</sub> solubility in slurry phase, when pressure is about 500 psi. A further increase in pressure does not show significant effect on the HDO process.

To conclude, HDO of pyrolysis oil over supported catalysts at mild condition with solvent dilution was successfully demonstrated as a promising way of upgrading to fuels. During HDO, self-polymerization was minimized and valuable products such as alcohols (up to 16%) and hydrocarbons (21%), which can be used as additive in gasoline and diesel fuels, were produced. These results demonstrated the possibility of transportation fuels by HDO of pyrolysis oil under mild conditions.

## **5.2.Recommendations for future work**

To continue the pathway of the research reported in this thesis, it is recommended that the following work be pursued. Since the HDO of pyrolysis is in H<sub>2</sub>-excess conditions and pressure

of 500 psig ensure solubility of hydrogen, the use of syngas or N<sub>2</sub> and H<sub>2</sub> mixture gas instead of pure H<sub>2</sub> may achieve same results. This can significantly lower the cost of H<sub>2</sub> usage. It will be ever better to recycle and reuse the exhaust gas that contains over 90% H<sub>2</sub>. Though noble supported catalysts are shown to be very successful in HDO, utilizing them at large scales may still be limited because of the difficulty of catalyst regeneration after pyrolysis oil upgrading. The Ru supported catalysts were shown to be the most active, and research is needed to synthesize less expensive catalysts or significantly improve the efficiency of current catalyst, such as nano-sized catalysts to decrease the catalyst loading for HDO. A process based on metal mediated pyrolysis oil upgrading to fuels by HDO will have commercial potential.

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## Appendix

### Chapter 2.

Pyrolysis oil upgrading runs with switchgrass-derived pyrolysis oil in a 300 mL batch reactor

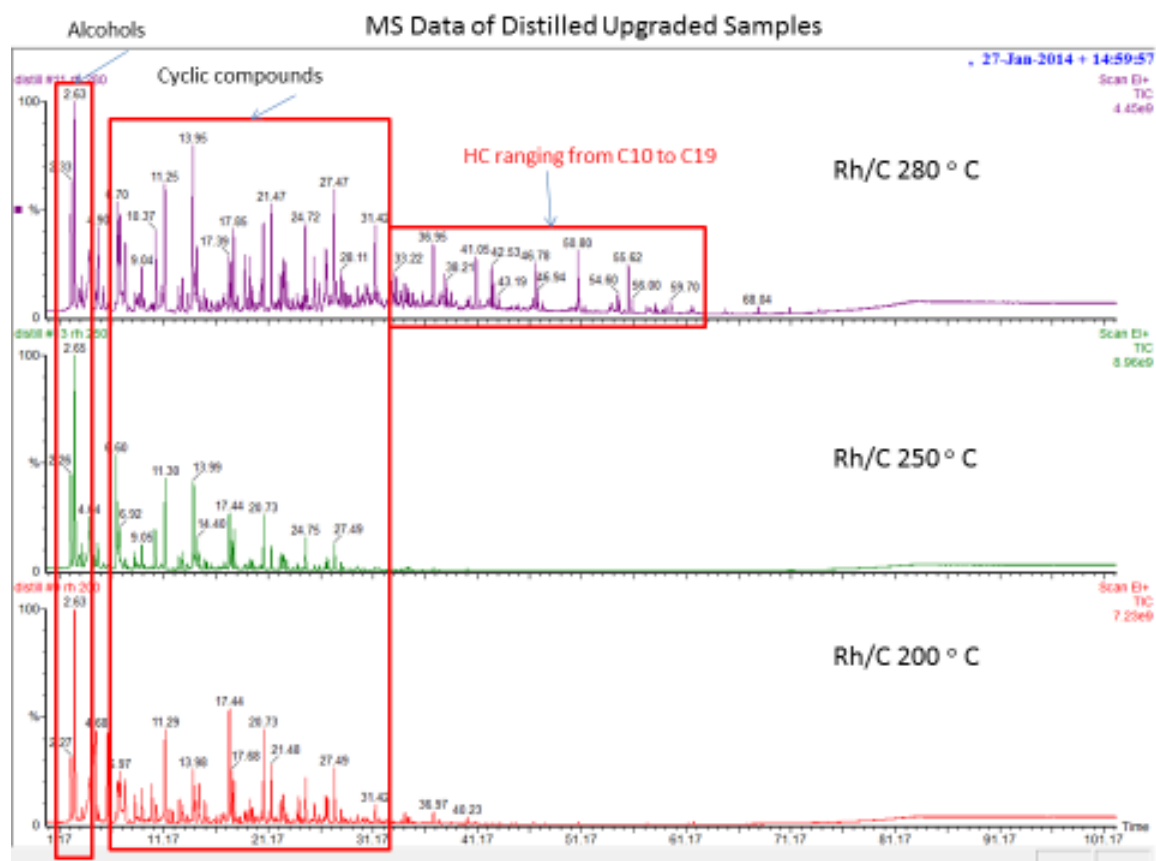
Run	Catalysts	Temperature	P(initial)	P(final)	$\Delta P$	Products Gas Composition			
		(°C)	(Psig)	(Psig)	(Psig)	CO <sub>2</sub> %	CO %	CH <sub>4</sub> %	H <sub>2</sub> %
1	Rh/C	200	535	509	26	0.612	0.070	–	98.012
2*	Rh/C	200	504	475	29	0.715	–	–	98.125
3	Rh/C	250	535	502	33	0.844	–	–	88.324
4	Rh/C	280	535	484	51	1.493	–	0.052	89.544
5	Rh/C	200	1000	973	27	0.355	–	–	98.243
6	Rh/C	250	1000	936	64	0.536	0.076	0.049	93.510
7	Rh/C	280	1000	936	64	1.850	0.388	0.090	98.330
8*	Rh/C	280	1004	944	60	1.321	–	0.112	96.375
9	Rh/C	280	300	261	39	2.174	0.407	0.246	86.073
10	Ru/C	200	300	293	7	1.170	0.106	–	96.285
11	Ru/C	200	535	489	46	0.582	0.063	–	95.865
12*	Ru/C	200	535	503	32	0.613	–	–	95.311
13	Ru/C	250	535	493	42	0.667	0.084	–	81.088
14	Ru/C	250	1000	955	45	0.698	0.092	0.064	82.200
15	Ru/C	280	535	467	68	0.890	–	0.058	85.374
16*	Ru/C	280	535	475	60	0.665	–	–	87.912
17	Ru/C	280	1000	893	107	0.630	0.134	0.054	91.720
19*	Ru/C	280	1000	853	147	0.593	–	0.064	93.773

20*	Ru/C	280	1000	887	113	0.687	0.122	0.056	93.655
21	None	280	1000	987	13	0.301	0.116	0.069	97.200

\*Repeated experiments

### Chapter 3.

Upgraded pyrolysis oil were distilled using micro-distillation setup at 120 °C.



Individual hydrocarbon product in distilled upgraded pyrolysis oil over Rh at 280 °C

<b>Compound</b>	<b>Retention Time (min)</b>	<b>Formula</b>	<b>Relative Area Percent (%)</b>
Dodecane	33.22	C <sub>12</sub> H <sub>26</sub>	0.467
Cis-3-Dodecene	33.44	C <sub>12</sub> H <sub>24</sub>	0.430
Trans-3-Dodecene	33.92	C <sub>12</sub> H <sub>24</sub>	0.318
Tridecane	38.02	C <sub>13</sub> H <sub>28</sub>	0.467
2-Tridecene	38.21	C <sub>13</sub> H <sub>26</sub>	0.379
6-Tridecene	38.68	C <sub>13</sub> H <sub>26</sub>	0.274
Tetradecane	42.53	C <sub>14</sub> H <sub>30</sub>	0.577
7-Tetradecene	42.71	C <sub>14</sub> H <sub>28</sub>	0.334
3-Tetradecene	43.19	C <sub>14</sub> H <sub>28</sub>	0.132
Pentadecane	46.78	C <sub>15</sub> H <sub>32</sub>	0.672
1-Pentadecene	46.94	C <sub>15</sub> H <sub>30</sub>	0.239
Hexadecane	50.80	C <sub>16</sub> H <sub>34</sub>	0.840
Cetene	50.94	C <sub>16</sub> H <sub>32</sub>	0.223
Heptadecane	54.60	C <sub>17</sub> H <sub>36</sub>	0.236
3,7,11,15- Tetramethyl-2- Hexadecene	55.62	C <sub>20</sub> H <sub>40</sub>	0.619

Individual alcohol product in distilled upgraded pyrolysis oil over Rh at 200, 250, 280 °C

<b>Compound</b>	<b>Group</b>	<b>Relative Area Percentage (%)</b>		
		<b>200 °C</b>	<b>250 °C</b>	<b>280 °C</b>
2-methoxy-ethanol	Alcohols	-	-	2.638
Butanol	Alcohols	-	-	0.641
Acetol alcohol	Alcohols	3.275	-	
Ethylene glycol	Alcohols	3.206	2.146	3.206
1-hydroxy-2-butanone	Alcohols	2.225	-	
Cyclohexanol	Alcohols	-	-	0.766
SUM of Alcohols		8.706	2.146	7.251
Cyclohexane	Hydrocarbons	-	-	4.329
Cyclopentanone	Cyclic Compounds	3.689	3.844	1.013