



# Experimental Analysis Of Hydrodeoxygenation And Dehydrogenation Of Bio-Oil

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## ABSTRACT

The study investigated the experimental analysis of hydrodeoxygenation and dehydrogenation of bio-oil. The study adopted the experimental research design. To upgrade bio-oil to transportation fuel which will be the apparent similarities between hydrodesulphurization (HDS) (a refinery process) and hydrodeoxygenation by applying the HDS catalysts such as NiMo/Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub> to the hydrodeoxygenation process. Higher temperatures and pressures are required for hydrodeoxygenation to avoid charring during the treatment of bio-oil. The use of nano-materials to remove unwanted constituents in bio-oil is another formidable method. Because of its unique properties such as acidity and micro porosity, the hydrogen type of the HZSM-5 catalyst with more robust acid pore sites and commonly used in different catalytic fields has been adapted for the catalytic upgrade bio-oil. Findings from table 1, research question 1, revealed that Carbon (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 71.5, 42.3 and 84.2-87.4 respectively. Also, Hydrogen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 7, 6.7 and 9.7-13.2 respectively. Further, Oxygen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 15, 48.1 and 0.1-0.6 respectively. Finally, Sulphur (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as <43, 23 and 0.004 respectively. Findings from research question 2, table 2, revealed that H/C atom ration for high pressure liquefaction is 1.2, 1.23 and 1.97 respectively. Also, for density (g/m) high pressure liquefaction is 1.15, 24.8 and 0.926 respectively. Further, for moisture (wt%), high pressure liquefaction is 5.1, 24.7 and 0.009 respectively. The study recommended that pyrolysis process is efficient for the production of upgraded bio fuel needed for most engines.

**Keywords:** Hydrodeoxygenation, Dehydrogenation, temperature, Bio-Oil, Pyrolysis

## INTRODUCTION

Despite the numerous bio-oil upgrading methodologies, significant research efforts in bio-oil upgrading development have focused on catalytic hydrogenation (Álvarez-Chávez, et al., 2019; Zhang, et al., 2019). The hydrotreatment process involves a stabilization step where reactive bio-oil compounds are converted to less active compounds to prevent severe hydrotreatment charring (Elliott, 2007). To upgrade bio-oil to transportation fuel, Elliott and Baker (1984) used the apparent similarities between hydrodesulfurization (HDS) (a refinery process) and hydrodeoxygenation by applying the HDS catalysts such as NiMo/Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub> to the hydrodeoxygenation process. Higher temperatures and pressures are required for hydrodeoxygenation to avoid charring during the treatment of bio-oil.

A significant challenge to the success of this strategy is that bio-oil is highly reactive, producing coke when heated, thereby deactivating the catalyst and blocking the reactor. Before upgrading using zeolite as catalysts, coke precursors such as aldehydes, oxyphenols, furfural, and lignin-derived oligomers are

removed to decrease coke production. In addition, it is better to use hydrogen-free or hydrogen-lean approaches since the cost of hydrogen is enormous. The use of nanomaterials to remove unwanted constituents in bio-oil is another formidable method. Because of its unique properties such as acidity and microporosity, the hydrogen type of the HZSM-5 catalyst with more robust acid pore sites and commonly used in different catalytic fields has been adapted for the catalytic upgrade bio-oil. This hierarchical microporous HZSM-5 zeolite can be improved in molecular sieve channels, although it is still limited by the diffusion of reactants (Wang, 2013).

The easily polymerized compounds such as lignin-derived phenols and furfural are effectively removed from bio-oil (Shi, et al., 2016). Furthermore, studies show that polymerization reaction during bio-oil storage is a continuous process between bio-oil components, leading to increased viscosity. Due to aging reactions, all bio-oils phase separate, resulting in an increase in the molecular weight and water-insoluble fraction, as well as carbonyl compound reactions resulting in a decrease in carbonyl content.

This correlates linearly with the average molecular weight and the content of aged oil carbonyl (Kim, et al., 2012). Unwanted aging reactions in bio-oil could be avoided through chemical and physical improvements such as solvent addition (Diebold & Czernik, 1997), emulsification with diesel fuel (Chen & Yoshikawa, 2018), deoxygenation using zeolite catalysts (Wang, et al., 2010), and catalytic hydrotreating (Tang, et al., 2009 ). The addition of water to the bio-oil will divide into two phases: a polar and lignin-extractive non-polar viscous bottom phase (Chen, et al., 2011). The use of torrefaction (Meng, et al., 2012; Van der Stelt, et al., 2011) or by controlling the conditions of pyrolysis (Dong, et al., 2012), or by using only a selective part of feedstock (Dong, et al., 2012; Demirbas, 2007; Ba, et al., 2004) to produce qualitative bio-oil is another treatment method.

Given the limitations of the methods described and the fact that much of the research in biomass pyrolysis has been focused on improving the bio-oil product of pyrolysis to generate transportation fuel compared with the fossil-derived fuels. However, to be commercially successful, biofuel technology must also produce high-value chemical or material co-products in addition to biofuels. In this case, the natural oxygen content we wanted to eliminate, might be beneficial since important oxygenated molecules like phenol and acetic acid are extracted as premium pharmaceutical precursors and other platform chemicals. As a result, this research used a solvent extraction model to separate chemicals (acetic acid and phenol) as valuable commodity chemicals in a bio-oil refining model. Additionally, the acetic acid recovered from the aqueous phase of bio-oil will be used in the chemical sector.

### **Aims of the Study**

The experimental analysis of hydrodeoxygenation and dehydrogenation of bio-oil was examined in this study. The study sought to:

1. Find out the status of high pressure liquefaction, flash pyrolysis and hydrogenated bio-oil on carbon, hydrogen, oxygen and sulphur.
2. Find out the H/C atom ratio (dry), density (g/ml) and moisture (wt%) of property of bio oil upgrade.

### **Research Questions**

The following research questions were developed and used as a guide for the study:

1. What is the status of high pressure liquefaction, flash pyrolysis and hydrogenated bio-oil on carbon, hydrogen, oxygen and sulphur?
2. What is H/C atom ratio (dry), density (g/ml) and moisture (wt%) of property of bio oil upgrade?

## **LITERATURE REVIEW**

### **Coke Formation**

In catalytic cracking of bio-oil, deactivation of the cracking catalyst, which results in relatively low yield in upgraded bio-oil products, is a crucial concern. The presence of coke on the reactor walls and catalyst might hinder the process of upgrading. The accumulation of char and soot on the reactor and catalyst surface causes deactivation. Furthermore, char deposition becomes more prominent while utilizing a fixed bed reactor. Add bio-oil with a hydrogen donor solvent such as methanol to boost the cracking process

and act as a diluent to the phenol fractions to avoid coke formation in hydrodeoxygenation. (Li, et al., 2014)

Literature shows that it was possible to attain a 100% conversion of guaiacol to yield 45.3% phenol and 11.1% cyclohexane, according to Attia(2020). Generally, coke formation during the upgrading of bio-oil is influenced by the catalyst's acidity and the feed type but is hardly affected by the reaction condition. As coke precursors are mainly aromatic hydrocarbons and coke formation is a consequence of polymerization and poly-condensation, improving the catalyst and extraction of phenolic from the bio-oil can minimize the development of coke.

### **Catalyst Deactivation**

The prolonging of catalyst service life during the upgrade of bio-oil is a matter that must be tackled for bio-oil upgrading to be cost-effective. Catalyst deactivation and regeneration are expensive as it involves gathering the deactivated catalyst and transporting them back to the manufacturer to regenerate them.

Catalyst deactivation is caused by :

- (i) moisture in the oil;
- (ii) sintering active sites;
- (iii) nitrogen, sulfur, and chlorine poisoning;
- (iv) metal deposition; and
- (v) Coke formation. The most important factors that cause catalyst deactivation are the formation of coke and water pollution (Attia, et al., 2020)

### **Fractionation of Bio-Oil**

The high viscosity of bio-oil makes it challenging to process, and the direct application as fuel is complex due to its inferior properties. The existence of organic compounds likes phenol and acetic acid in bio-oil is the primary source of the inferior properties such as rapid polymerization on storage and high acidity. The separation of bio-oil into its component parts is the pedestal upon which the efficiency of bio-oil upgrading to transportation fuel stands. Therefore, organic acids and phenolic components which have incredible demand in the global market must be extracted as platform chemicals to reduce the level of polymerization and acidity in the oil and this is an option to decrease the cost of the bio-oil upgrade.

Most oxygenates including acetic acid and phenol distributed into the aqueous and organic phases of the phase-separated bio-oil offer attractive commercial opportunities when extracted and purified. Bio-oil primary separation approaches include membrane separation, activated carbons, nano filtration (Teella, et al., 2011 ), physical liquid-liquid extraction (Vitasari, et al., 2012), and reactive extraction (Vitasari, et al., 2012), and crystallization. Acetic acid is an essential chemical reagent primarily employed in cellulose acetate and polyvinyl acetate production. Acetic acid and phenol could be isolated from the bio-oil to upgrade the bio-oil further. However, most purification processes fail to implement due to bio-oil's extreme complexity and reactivity. Various solvents extract bio-oil components, including water, ethyl acetate, paraffin, ether, and several others. Other special solvents such as CO<sub>2</sub> are also being utilized. The ability to select a suitable extraction solvent will ensure the excellent separation of the bio-oil into its constituent part. According to Hong et al. ( 2001), the use of conventional liquid-liquid extraction method for acetic acid offers low extraction efficiency and therefore unsuitable. Other studies have shown that direct distillation to isolate these chemicals from bio-oil is also not feasible due to the poor thermal stability of the oil (Oasmaa, et al., 2011). Also, direct extraction with an organic solvent is not attractive as a certain amount of the solvent ends up in the pyrolyzed oil phase (Li, et al., 2016; Mahfud, et al., 2008).

Nevertheless, reactive liquid-liquid extraction using tertiary amines, due to its selectivity and efficiency, has also been extensively studied for acetic acid recovery from aqueous solutions, including bio-oil. A combination of efficient extraction methods and suitable upgrading processes is imperative for bio-oil to be cost-competitive. But the regeneration of the tertiary amines by vacuum distillation leads to the loss of 2-ethyl hexanol, which can evaporate along with the solute.

## METHODOLOGY

The study adopted the experimental research design. This is because samples were drawn from the laboratory. The hydro treatment process involves a stabilization step where reactive bio-oil compounds are converted to less active compounds to prevent severe hydro treatment charring. To upgrade bio-oil to transportation fuel was used which is similar to the apparent similarities between hydrodesulphurization (HDS) (a refinery process) and hydrodeoxygenation by applying the HDS catalysts such as NiMo/Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub> to the hydrodeoxygenation process. Higher temperatures and pressures are required for hydrodeoxygenation to avoid charring during the treatment of bio-oil.

A significant challenge to the success of this strategy is that bio-oil is highly reactive, producing coke when heated, thereby deactivating the catalyst and blocking the reactor. Before upgrading using zeolite as catalysts, coke precursors such as aldehydes, oxyphenols, furfural, and lignin-derived oligomers are removed to decrease coke production. In addition, it is better to use hydrogen-free or hydrogen-lean approaches since the cost of hydrogen is enormous.

The use of nano-materials to remove unwanted constituents in bio-oil is another formidable method. Because of its unique properties such as acidity and micro porosity, the hydrogen type of the HZSM-5 catalyst with more robust acid pore sites and commonly used in different catalytic fields has been adapted for the catalytic upgrade bio-oil. This hierarchical microporous HZSM-5 zeolite can be improved in molecular sieve channels, although it is still limited by the diffusion of reactants.

## DATA ANALYSIS

**Research Question 1:** *What is the status of high pressure liquefaction, flash pyrolysis and hydrogenated bio-oil on carbon, hydrogen, oxygen and sulphur?*

Table 1: The status of high pressure liquefaction, flash pyrolysis and hydrogenated bio-oil on carbon, hydrogen, oxygen and sulphur.

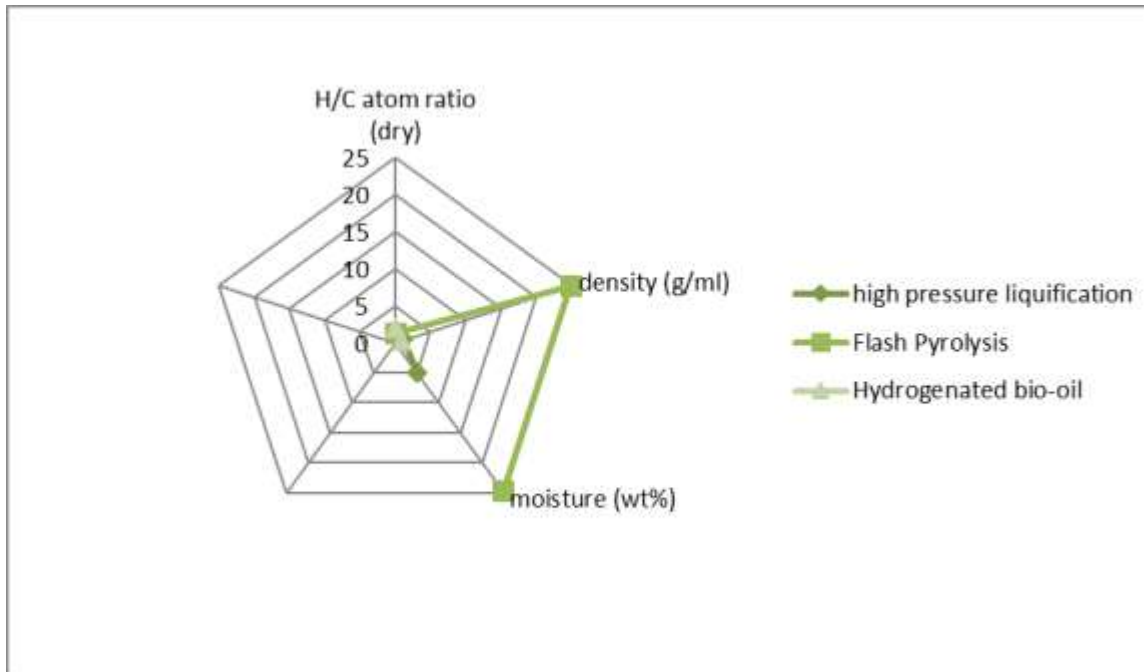
S/No	Items	High Pressure Liquefaction	Flash Pyrolysis	Hydrogenated bio-oil
1	Carbon (wt%)	71.5	42.3	84.2-87.4
2	Hydrogen (wt%)	7	6.7	9.7-13.2
3	Oxygen (wt%)	15	48.1	0.1-0.6
4	Sulphur (wt%)	<43	23	0.004

Findings from table 1, research question 1, revealed that Carbon (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 71.5, 42.3 and 84.2-87.4 respectively. Also, Hydrogen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 7, 6.7 and 9.7-13.2 respectively. Further, Oxygen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 15, 48.1 and 0.1-0.6 respectively. Finally, Sulphur (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as <43, 23 and 0.004 respectively.

## Research Question 2

*What is H/C atom ratio (dry), density (g/ml) and moisture (wt%) of property of bio oil upgrade?*

Table 2: H/C atom ratio (dry), density (g/ml) and moisture (wt%) of property of bio oil upgrade



Findings from research question 2, table 2, revealed that H/C atom ration for high pressure liquefaction is 1.2, 1.23 and 1.97 respectively. Also, for density (g/m) high pressure liquefaction is 1.15, 24.8 and 0.926 respectively. Further, for moisture (wt%), high pressure liquefaction is 5.1, 24.7 and 0.009 respectively.

### Summary of Findings

Below are the summary of the findings:

- Findings from table 1, research question 1, revealed that Carbon (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 71.5, 42.3 and 84.2-87.4 respectively. Also, Hydrogen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 7, 6.7 and 9.7-13.2 respectively. Further, Oxygen (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as 15, 48.1 and 0.1-0.6 respectively. Finally, Sulphur (wt%) had a High Pressure Liquefaction, Flash Pyrolysis and Hydrogenated bio-oil data as <43, 23 and 0.004 respectively.
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### CONCLUSION

The study concluded that the hydrogenation of aromatic components should be minimized otherwise it would lead to the reduction of octane number and the increasing of H<sub>2</sub> consumption. During hydro processing, both of the energy content and the stability of the fuel are substantially increased.

### RECOMMENDATIONS

The study recommended that pyrolysis process is efficient for the production of upgraded bio fuel needed for most engines.

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