Liquid Fuel Production from Biomass Tar by Hydrogenation

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Abstract— Bio - oils production studied from heavy tar which is organic phase of pyrolysis oil using CoMo/Al2O3 catalyst in the bench scale hydrogenation process. In this experiments, hydrogenation of biomass tar were carried out in varied reaction conditions to elucidate influence of operation factors. The effect of reaction temperature, retention time, feed rate, space velocity (SV), hydrogen concentration, and catalyst loading factor on bio-oil yield, carbon content, and carbon recovery of heavy tar by catalytic conversion was investigated. The six variables ranged from 300 to 500 °C for temperature, 0-140 min for retention time, 1,2, and 3.3 g-tar/min for feed rate, 0.1, 0.2, and 0.4 s-1 for SV, 25, 50, and 75 v% for hydrogen concentration, and 1.3, 2.7 and 4.4 mg-tar/min/g-cat for catalyst loading factor. The product oils and gaseous species were analyzed by Karl Fischer moisture titrating analyzer, Total organic carbon (TOC) analyzer, GC – 14A gas chromatography, Agilent 3000 micro gas chromatography and elemental analysis. It was found that maximum bio-oil yield of 29wt% was obtained at 400°C, 60-140 min, 2 g-tar/min feed rate, 0.2 s-1 SV, 50 v% hydrogen concentration and 2.7 mg-tar /min/g-cat catalyst loading. In this study, it was able to produce a high quality liquid fuel with minimum water content 0.3wt% in oil phase and maximum level of HHV (39.8MJ/kg). The oil was also observed to have an abundant amount of aromatic compounds. It was possible to produce multi-component fuels through the hydrogenation of bio-oils from heavy tar.

Key words— Bio-oil, Bio-oil yield, Catalytic conversion, CoMo/Al2O3 catalyst, Heavy tar

I. INTRODUCTION

Today there is a worldwide interest in the use of biomass as an environmental friendly renewable energy source. Many concerns point out to the need to use of renewable feedstock, composing the energetic matrix and replacing as much as possible the fossil fuels; among them could be mentioned the depletion of fossil oil reserves, constant uncertainties as far as price is concerned, unsecured supplies, and environmental pollution. Greenhouse effect and its consequences on climate change is one of the drawbacks resulting from the extensive use of this kind of fuels. These problems require the development of new alternative fuels such as biofuels. Biomass is a potential energy resource and there are several pathways (e.g. physical, thermal, chemical, and biological conversion) to generate energy from biomass. By the preceding methods, biomass could be converted to heat, electricity, solid fuels (coal), liquid fuels (bio-oil, methanol and ethanol) and gas fuels (hydrogen and syngas), respectively.

In the near term, biomass is the most likely renewable organic substitute to petroleum. Biomass is a renewable material containing appreciable quantities of hydrogen, oxygen and carbon. It is available from a wide range of sources such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (i.e. switch grass), waste paper, corn, and many more. For hydrogen and syngas productions, the current biomass technologies include: pyrolysis, gasification, reforming (the most studied by researchers worldwide) and combustion. The pyrolysis of biomass without catalyst is a very simple and a cheap method for energy conversion. Pyrolysis is also a previous step to other thermo conversion processes, such as combustion and gasification. Valuable gases, such as hydrogen and carbon monoxide, can also be generated by pyrolysis.

This paper aims to give methods of hydrogenation liquefaction and liquid fuel production from heavy tar and their potential of development.

II. EXPERIMENTAL SECTION
A. Biomass Feedstock

Heavy tar, which is organic phase of pyrolysis oil was used as a feedstock in this hydrogenation process. Heavy tar used in this research was obtained from pyrolyzer in pilot scale three compartment internal circulating fluidized beds. The characteristics of heavy tar were carried out. The proximate analysis was done using ASTM method to determine the ash content, volatile matter content and fixed carbon content. While the moisture content of heavy tar was determined using Karl Fischer Moisture Titrating analyzer (MKA-610). Ultimate analysis of heavy tar was performed using an elemental analyzer (JMA-Auto Sampler 1000). In this experiment, CoMo/Al2O3 catalyst (HD Max 201 TRX 2.5, hydrotreating catalyst) was used.

III. EXPERIMENTAL SETUP

The experiments were conducted using a fixed – bed reactor in a batch process at atmospheric pressure. The height and inside diameter of the reactor were 558 and 152 mm

respectively. Two fluids nozzle was used in the evaporator. CoMo/Al2O3 catalyst was used in this study. Figure 1 showed the schematic diagram of experimental apparatus. This unit consists of burner, fixed – bed reactor, thermocouple to control the top and bottom temperature, feeder machine to supply the specified amount of feedstock into the reactor, gas flow meters to supply gases such as hydrogen, nitrogen and hydrogen sulfide, liquid collector to trap total liquid products, dry test gas meter and gas collection bags.
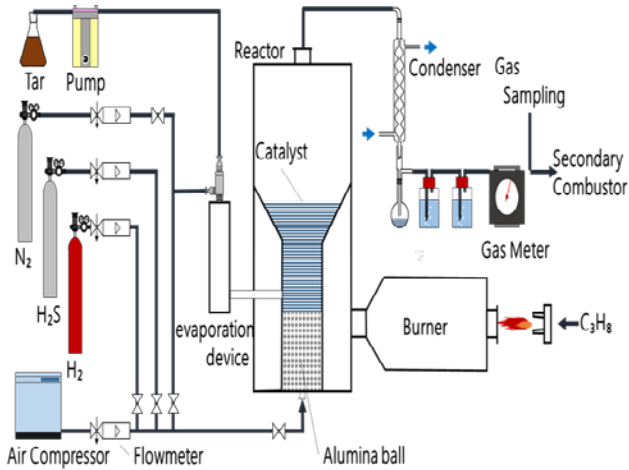

Figure 1: Schematic diagram of experimental apparatus

The experiment was started by heating the catalyst at 200 °C for 60 min to obtain anhydrous conditions. Then, the temperature was set to the desired value (300 – 500)°C in a stream of nitrogen at a heating rate of 10 °C/min. When the temperature of the reactor was reached, hydrogen, nitrogen, and hydrogen sulfide gases flow to the reactor. Experiments are performed at three gas flow rate (6, 12, 24) l/min. The organic phase (heavy tar) was injected into the vertical reactor at a feed rate of (1, 2, 3.3) g/min using a peristaltic pump. Each run lasted for about 30 min and longer time and was performed in triplicate.

During the process, the organic phase was evaporated due to the effect of the thermal conversion at reactor temperature. As the initial effect of the thermal reaction, a solid residue was formed on the top layer of quartz wool, derived from some of the ingredients of the organic phase. Furthermore, the vapors from the evaporation of the organic phase flowed downward and into contact with the catalyst, after which it passed through the cooler tube at 5 °C and finally flowed into a trap apparatus to condense as a liquid product. As a consequence, impurities were deposited on the surface of the catalyst and the presence of coke was indicated.

In this experiment, the amount of noncondensable gases was determined by the difference between the total weights of the organic phase (feed) and other products (oil, water, char, and coke). The liquid product was obtained in two immiscible layers defined as the oil and water fractions. The oil can be easily separated from the water fraction using a micropipette. After separation, each fraction was weighed separately, and the obtained values were then calculated using equation 1.Figure 2 showed liquid products with two immiscible layers from this experiment.

$$\text{Yield (wt\%)} = \{product(g)/feed(g)\} \times 100\% \qquad Eq.1$$

Figure 2: Liquid products with two immiscible layers

The gas produced during hydrogenation process was collected in gas collection bag. The gas in the collection bag was analyzed using GC – 14A gas chromatography and Agilent 3000 micro gas chromatography.

IV. EXPERIMENTAL CONDITION

Table 1 showed hydrogenated gasification experimental conditions with H2S, 300ppm. This table was based on orthogonal design. We considered in three levels with hydrogen sulfide, nine experiments are totally required. Experiments were performed at three temperatures (300,400,500) °C using bench scale hydrogenation reactor.

TABLE I: HYDROGENATED GASIFICATION EXPERIMENTAL CONDITIONS (H2S, 300PPM)

EXP: NO.	SV, s-1	TEMP, °C	FEED RATE, G-TAR/MIN	CATALYST LOADING, KG-CAT	CATALYST LOAD, MG-TAR/MIN/G-CAT	H2 CON, V%	TOTAL GAS FLOW, L/MIN	H2, L/MIN	N2, L/MIN	H2S, L/MIN	RETENTION TIME, MIN
1	0.1	300	1	0.8	1.3	25	6	1.5	3.9	0.6	35
2	0.2	300	2	0.8	2.7	50	12	6	4.8	1.2	40
3	0.4	300	3.3	0.8	4.4	75	24	18	3.6	2.4	30
4	0.1	400	3.3	0.8	4.4	50	6	3	2.4	0.6	70
5	0.2	400	1	0.8	1.3	75	12	9	1.8	1.2	60
6	0.4	400	2	0.8	2.7	25	24	6	15.6	2.4	30
7	0.1	500	2	0.8	2.7	75	6	4.5	0.9	0.6	60
8	0.2	500	3.3	0.8	4.4	50	24	12	9.6	2.4	30
9	0.4	500	1	0.8	1.3	25	12	3	7.8	1.2	70

Moreover, experiments were carried out that it becomes catalyst temperature 400°C, SV 0.2 s-1 , H2 concentration 50 v% and catalyst loading factor 2.7 mg-tar /min/g-cat. Experimental conditions were shown in Table 2. It was used in our experiments because it has an obvious effect on the reaction with hydrogen sulfide additives.

TABLE II: LIQUID PRODUCTION EXPERIMENTS UNDER AN APPROPRIATE OPERATING CONDITION

Exp: No.	SV , s-1	Temp , °C	Feed rate, g-tar/min	Catalyst load, mg-tar/min/g-cat	H2 Con, v%	H2S (3%), L/min	Retention time , min
1	0.2	400	2	2.7	50	0.12	0-30
2	0.2	400	2	2.7	50	0.12	30-60
3	0.2	400	2	2.7	50	0.12	60-140

V.   RESULTS AND DISCUSSION

A.   Nine of Each Experimental Result

The results obtained from nine of each experiment were presented in Table 3. As a result of carrying out nine sorts of experiment using the orthogonal table arranged by three levels with addition or without hydrogen sulfide, we confirmed an efficacy of hydrogen sulfide in almost all sorts of experiment in case of a hydrogen sulfide addition. Also we found out that there was an effect on high temperature side from the temperature of catalytic layer in a result of an oxygen content and energy recovery rate.

TABLE III: NINE OF EACH EXPERIMENTAL RESULT

Exp: No.	Oxygen Content (wt% - d.a.f)	Carbon Balance(oil) (wt% - C)	Fuel Recovery Rate (wt% - tar)	Energy Recovery Rate (% - tar)
1	24.7	33.9	38.7	34.1
2	27.6	26.9	37.3	26.3
3	31.5	25.8	34.3	25.6
4	27.7	6.1	7.7	6.0
5	14.0	42.7	42.8	42.2
6	13.0	65.5	72.3	63.9
7	19.0	18.6	24.5	17.9
8	14.3	56.2	66.5	53.7
9	9.6	46.8	45.1	45.4

The main purpose of experiment was to remove oxygen compounds in the oil phase. We observed that oxygen content of oil phase less than 10wt%. The presence of H2S strongly decreased the hydro de - oxygenation (HDO) activity of the sulfided catalyst, and the ratio of the HDO reaction pathways depended on the H2S concentration. The effect of H2S addition on the activity and the stability of CoMo catalyst during hydrotreating of heavy tar were studied. A minimum concentration of hydrogen sulfide was usually required to maintain the catalyst in the sulfided state. In addition to desulfurization and changes in the structure of the active sulfided catalyst, the formation of coke and high molecular weight compounds on the catalyst decreased its activity but did not affect the selectivity of HDO. Figure 3 showed O/C and H/C ratios of hydrogenated gasification by H2S free and with 300ppm of H2S.
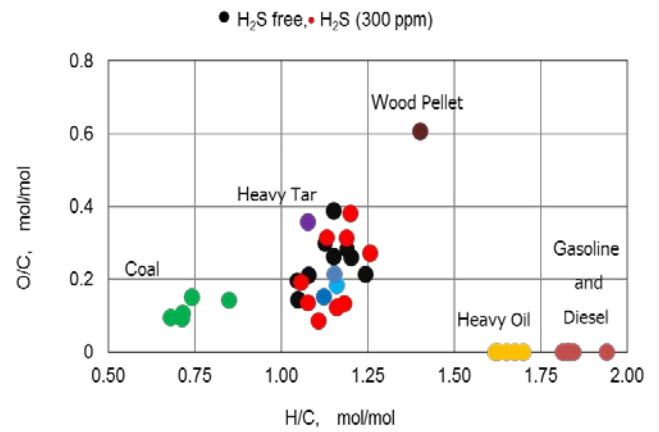

Figure 3: O/C and H/C ratios of hydrogenated gasification

The each factor's effect for the hydrogenated gasification was found to be different by H2S free and with 300ppm of H2S. From the point of energy, the result with addition of 300ppm of H2S was better than that of H2S free. Moreover, it would be necessary for the future to find the optimum experimental conditions and feedstock in order to improve O/C and H/C ratios of product liquid fuels that of heavy oil.

B.   Liquid Production Experiments under An Appropriate Operation Results

Table 4 showed liquid production experiments under an appropriate operation results.

TABLE IV: LIQUID PRODUCTION EXPERIMENT UNDER AN APPROPRIATE OPERATION RESULTS

Exp: No.	Oil yield , wt%	Water content in oil phase, wt%	HHV, MJ/kg	Oxygen content, wt%	Carbon content, wt%	H/C, mol/mol	O/C, mol/mol
1	4	1.6	36.7	9.66	83.06	1.0	0.1
2	13	1.5	39.8	4.48	88.02	1.0	0.0
3	29	0.3	39.3	5.75	86.66	1.0	0.0

B.1.Product Yields
The result of product yields from heavy tar after Hydrogenation at 400°C was shown in figure 4.Hydrogenation process generate four products including a fuel-like oil, an aqueous phase liquid, non-condensable gases and coke. Bio oil yields ranged from approaching 4to 29wt%, depending on the temperature and reaction time (our target to produce maximum oil yield). By-product yields including non-condensable gas, aqueous phase liquid and coke were decreased to longer time. So, longer time H2S injection was taken liquid fuel yield increase and decrease of water content.
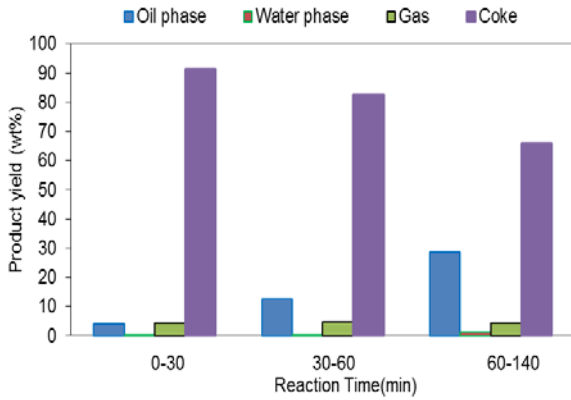
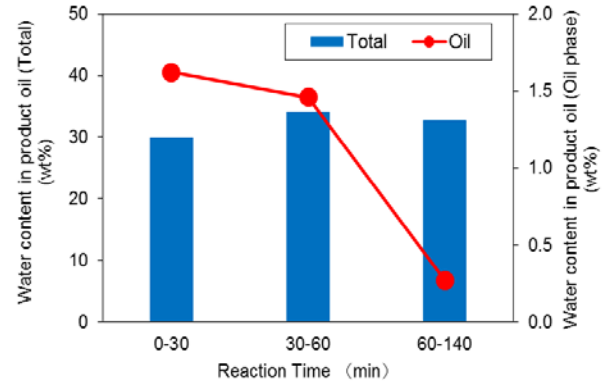Figure 4: Yield of products from heavy tar after Hydrogenation at 400°C

B.2. Carbon Balance

The result of carbon conversion from heavy tar was shown in figure 5.   Carbon amount of products oil can be measured by the analysis of their respective products. It is hard to obtain coke so carbon amount of coke can be calculated and estimated by various methods as follows: C (coke) = 100 – [C (gas) + C (oil phase) + C (water phase)]. C (coke) is the amount of carbon included in cokes. C (gas) is the amount of   carbon included in gas. C (oil phase) and C (water phase) are the amounts of carbon included in bio-oil.
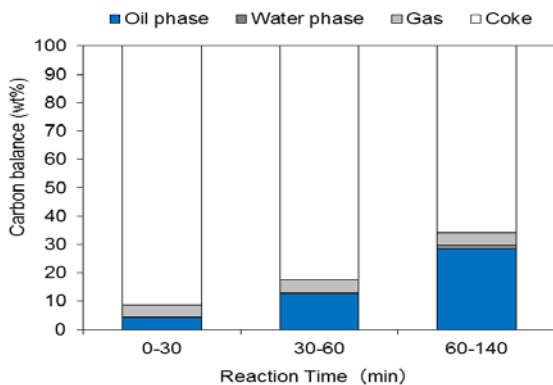

Figure 5: Carbon conversion of heavy tar after Hydrogenation at 400°C

B.3. Water Content

 The result of water content for product oil was shown in Figure 6. According to this result, the total oil product has about 30% of water content and it was observed that the amount of water content was decreased with the increasing of reaction time in the case of just only focusing on the oil phase. Minimum water content contained 0.3wt% in oil phase compared to total product oil. The decrease of water content occurred catalyst regeneration by the formation of hydrocarbons. Moreover, reports written by Sharma and Bakhshi et al. showed also that approximately (2-5) wt% a small amount of water was remained in the total product oil after catalyst regeneration.

Figure 6: Water content in product oil after Hydrogenation at 400°C

B.4. Higher Heating Value (HHV)

HHV was an essential parameter for determining the amount of energy content of fuel. The highest HHV obtained was 39.8MJ/kg take one's time (30-60) min compare to 36.7MJ/kg take one's time (0-30) min by using Dulong equation. Higher heating value was increased 10% from 36.7 to 39.8 MJ /kg. HHV of Wood pellet (18.8 MJ/kg) compare to product oil (39.8MJ/kg) so that it was shown approximately double efficiency.   Bio-oil's HHV is usually between 36 and 40 MJ/kg. The result of HHV was shown in figure 7.

Figure 7: Higher heating value of each item

B.5. Elemental Analysis

The result of elemental analysis in oil phase was shown in Table 5. The main purpose of this experiment was to remove oxygen compounds in oil phase which has increasing effect of hydrocarbon compounds. We observed that oxygen content of oil phase less than 10wt%. Oxygen content was decreased to

about 4.48wt%. Carbon content of oil phase was quite higher than that of heavy tar. It was observed that sulfur and nitrogen contents were lower in all oil products.

TABLE V: RESULT OF ELEMENTAL ANALYSIS IN OIL PHASE

Sample	Time	Elemental Analysis (wt%)			
		C	H	N	O
1	0-30	83.06	7.11	0.00	9.66
2	30-60	88.02	7.51	0.00	4.48
3	60-140	86.66	7.59	0.00	5.75

B.6. H/C and O/C Ratios of Product Oil

When oil is used as fuel, it is important to determine ratios of atomic H/C and O/C. Generally, increase of H/C ratio results in high value products such as gasoline. However, increase of O/C ratio brings out a converse result as well. Duman et al. reported that activity effect of de-oxygenation in catalytic cracking is favorable and causes increase of H/C ratio. There was observed no change in H/C ratio of product oil. It was observed that O/C ratio decreased a little with increasing of reaction time. Some studies also reported that low H/C ratio describes increase of aromatic compounds in oil products. O/C ratio very close to that of gasoline, but H/C ratio far from gasoline however, product oil used as transportation fuel. The result of H/C and O/C ratios in oil phase was shown in figure 8.
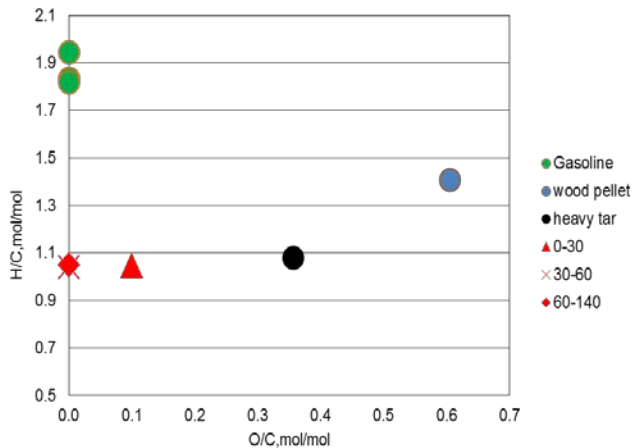

Figure 8: H/C and O/C ratios of product oil

VI.   Conclusion

This research showed that the recovery of liquid fuel from heavy tar, which is organic phase of pyrolysis oil was successfully performed using a catalytic conversion. This experiment also confirmed that the temperature and reaction time have a significant effect on the distribution of product yields obtained from the catalytic conversion. A temperature of around 400 °C and longer time were found to be most suitable for catalysts to perform the de-oxygenation activity, which Meiktila Township, Myanmar , moethandakyi@gmail.com

caused an increase in the production of water and gas. In this study, it was able to produce a high quality liquid fuel with minimum water content 0.3wt% in oil phase and maximum level of HHV (39.8MJ/kg). The oil was also observed to have an abundant amount of aromatic compounds. Finally, we concluded that the characteristics of product oil were very close to those of gasoline and that the product oil has the potential to be used as a transportation fuel.

REFERENCES

[1] G. W. Huber, S. Iborra and A. Corma, Chem. Rev., 2006, 106, 4044–4098.

[2] Faisal Abnisa, W. M. A. Wan Daud, Arash Arami-Niya, Brahim Si Ali, and J. N. Sahu, Energy Fuels 2014, 28, 3074−3085..

[3] Juan Carlos Serrano-Ruiz and James A. Dumesic, Catalytic Production of Liquid Hydrocarbon Transportation Fuels, Department of Chemical and Biological Engineering, University of Wisconsin—Madison, Madison, WI 53706, USA,2012.

[4] Elliott DC (2007) Historical developments in hydro processing bio-oils. Energy Fuel 21:1792–1815 63.Furimsky E (2000) Catalytic hydrodeoxygenation. Appl Catal A Gen 199: 147–190.

[5] Czernik S, French R, Feik C, Chornet E (2002) Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermo conversion processes. Ind Eng Chem Res 41:4209–4215.

[6] Cortright RD, Davda RR, Dumesic JA (2002) Hydrogen from catalytic reforming of biomass derived hydrocarbons in liquid water. Nature, 418:964–967.

[7] Davda RR, Dumesic JA (2004) Renewable hydrogen by aqueous-phase reforming of glucose. Chem Commun 36–37.

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