

## CATALYZED LIQUEFACTION OF EMPTY PALM FRUIT BUNCH (EPFB) IN SUB-CRITICAL WATER

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### ABSTRACT

Effect of alkaline catalysts (NaOH, KOH & K<sub>2</sub>CO<sub>3</sub>) on EPFB biomass liquefaction is investigated under sub-critical water conditions in a batch type reactor operating at 270°C and 20 bars for a period of 20 minutes. In this study catalyst performance and suitable biomass to water ratio in order to support higher EPFB conversion, liquefied hydrocarbon yields and lignin degradation were screened. According to the results through GC-MS, FTIR, and UV spectrometer, one typical run could achieve 68 % of liquid hydrocarbons with 72.4 % EPFB conversion and 65.6 % lignin degradation in 1.0 M and 2:10 biomass to water ratio operating at the above said conditions. Liquid output was only 36.4 % when subjected to the same operating conditions in the absence of catalyst. Furthermore, high biomass to water ratios beyond 2:10 decreased both solid mass conversion and liquid hydrocarbons. The order of the catalyst reactivity was in the following order: K<sub>2</sub>CO<sub>3</sub> > KOH > NaOH. Phenols and esters were dominant in the liquid products and K<sub>2</sub>CO<sub>3</sub> yielded the highest value of phenols. The alkaline catalyzed process assisted with hot water treatments seemed promising for production of phenolic-rich bio oils from EPFB.

### 1 INTRODUCTION

Biomass supplies 12-14 % of energy requirements worldwide and shares around 35-50 % in developing countries. Furthermore, fossil energy depletion and its uneconomical extraction have spurred the idea of utilizing biomass in various applications like bio-fuels and bio-chemicals. It is widely accepted that utilizing biomass as energy source would bring forth social and economical benefits in less developed regions of the world. Other benefits include i) sustainable energy through renewable biomass ii) CO<sub>2</sub> neutral substitute of

fossil fuel iii) reduction in gases like NO<sub>x</sub>, SO<sub>x</sub> due to less sulfur and nitrogen contents present in biomass and iv) abundant availability in all regions of world (Demirbas et. al. 2000, Kucuk et. al. 1997 Mckendry et. al. 2002). Empty palm fruit bunch (EPFB)-biomass used in current study, is one of the major wastes of oil palm plantations. EPFB amounts to 4.4 tonnes per hectare per year, approximately concedes 20.4 % of total oil palm biomass. Total 73.4 million tonnes of palm biomass, in Malaysia for example, supplies 14.89 million tonnes I:FB and 37.65 million tonnes world wide on yearly basis (Tau et. al. 2007, Yang et. al. 2004). Converting cheap abundant amounts of renewable palm EFB into valuable commodities like bio-fuels would bring forth energy security and social benefits in countries like Malaysia, Indonesia, Thailand and tropical African countries.

Liquefaction of biomass feedstock to liquids like bio-fuels and chemicals, is one of the major alternatives for biomass utilization (Chunbao et. al. 2008, Mohan et. al. 2006, Bridgewater et. al. 1995, 2001). Biomass is liquefied into fuels and chemical based commodities through thermal, thermochemical, biochemical and biological routes. Biological means are quite economical for such liquefactions yet very low conversion of solid mass makes these processes unfit for large scale applications. Conversely, liquid yield is quite high (50-70 %) in thermal and thermochemical processes. However still issues like low product quality, high temperatures and pressures daunt industrial applications of such processes. In thermochemical methods, direct and indirect conversions are two viable options for biomass liquefaction.

Bio fuels and chemicals can be obtained indirectly from biomass gasification via Fischer-Tropsch conversion (Mark et. al. 2004, Charlo et. al. 2004) while direct processes like pyrolysis, extractions, and hydrogenations convert biomass solid to liquids. Direct processes are suitable choices in recent times due to

simpler processing steps permitted with post-processing of liquid oils in order to increase fuel value. However, selection of a suitable process depends on various factors-biomass types, product utility, economic aspects, and environmental conditions etc (Chunbao et. al. 2008, Peter et. al. 2002). Fast pyrolysis, wherein biomass is heated rapidly within 400- 850°C at atmospheric pressure usually, has reputation of yielding high amounts of products. However, problems like high water contents in product liquids, chars and a well mixed amount of organic compounds lower product quality and its potential application. Sub and supercritical extraction of biomass in solvents like water, methanol, ethanol, ether and CO<sub>2</sub> etc produces bio oil dominated by phenols and esters etc. Thus, super/sub critical liquefaction may be a suitable option for EPFB liquefaction for which current study is carried out.

The effect of catalysts like NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH, and K<sub>2</sub>CO<sub>3</sub> was studied on sub critical water liquefaction of woody biomass at 208°C (Selhan et. al. 2005). Uncatalyzed liquefaction of *Cunninghamia Lancelolata* in water medium yielded 24 % of liquid oils at 280-360°C and 8 gm biomass/100 mL water conditions (Yixin et. al. 2003). In another development, rice straw liquefaction in presence of various liquids like water and ethanol, 2-propanol under low temperature and pressure was studied (Yuan et. al. 2007). Depolymerization of lignin by alkali at 290°C in supercritical methanol illustrated lignin decomposition was proportional to base strength (Miller et. al. 1999). Effect of temperature on liquefaction of woody biomass in presence of Na<sub>2</sub>CO<sub>3</sub> catalyst within 280-420°C was studied and 380°C as the optimal temperature was recommended (Yejian et. al. 2007). Water-phenol solvent system to liquefy wood biomass at moderate 250°C in presence of catalysts like NaOH, CuSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was studied to investigate the effect of catalyst concentration, biomass to solvent ratios, pH of mixture and biomass types on liquids and residues production (Maldas et. al. 1996).

In this work, empty palm fruit bunch (EPFB) was liquefied in hot water at moderate operating conditions (200°C, 20-40 bars) and 20 minutes in presence of KOH, K<sub>2</sub>CO<sub>3</sub>, and NaOH catalysts to compare liquid yields and biomass conversions in catalytic and non-catalytic runs. Liquids and solids compositions as well as lignin decomposition were analyzed through GC-MS, FTIR and UV Spectrophotometer. The objectives of this work were to investigate effect of base catalysts and suitable EPFB/water ratio to produce bio-chemical rich bio oil.

## 2 EXPERIMENTAL

### 2.1 Materials

Empty palm fruit bunch (EPFB) was collected from FELDA oil palm company in Bukit Besar Kulai, Malaysia. The feed biomass was grounded to particle size ranged from 0.5 mm to 1.0 mm. Sulphuric acid and alkaline catalysts were obtained from Mallinckrodt Chemical Inc., USA and Quality Reagent Chemicals (QREC), NZ, respectively.

### 2.2 Hydro-liquefaction

The experimental rig consisted of a stainless steel autoclave, an electrical furnace and a product recovery system supported by water cooled condenser as shown in figure 1. Catalyst and crushed EPFB were mixed with water in a specified biomass to water ratio in the autoclave. Temperature, 270°C and pressure, 20-45 bars were maintained for 20 minutes residence times in this base catalyzed hot water liquefaction of EPFB. During reaction small quantity of gas was purged in a sampling tube in order to control pressure and avoid vapors loss. After 20 minutes of heating at 270°C, the operation was halted and cooled in open atmosphere followed by water cooling. Collected product was separated as unconverted solid mass and liquid portions. Effective biomass to water ratio, effect of basic catalysts and its concentration, were parameters notified in the above said procedure.

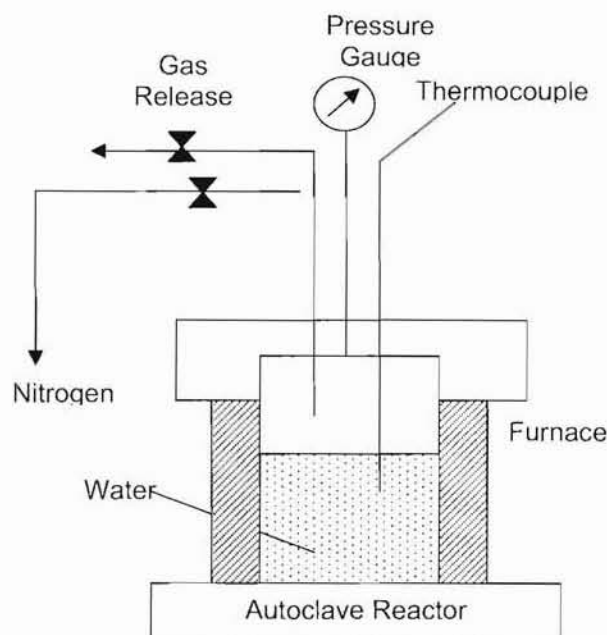


Fig. 1 Experimental setup

### 2.3 Analysis

#### 2.3.1 Kappa Number Test

In this experiment, the kappa number was derived from the ratio of the absorption spectral intensities at 546 nm wavelength measured at the beginning and end of the reaction of EPFB with permanganate through UV spectrophotometer analysis. Details of procedure can be followed elsewhere (Chai et al. 2000). Kappa number was calculated according to the following formula:

$$K = \frac{a}{w} \left( 1 - \frac{A^c}{A^o} \right)$$

Where K = Kappa number, a = Volume of 0.02mol/L permanganate solution used in experiment, w = Mass in grams of the solid sample used, A<sup>c</sup> = Spectral intensities of blank solution, A<sup>o</sup> = Spectral intensities of solution with the solid product

### 2.3.2 FTIR analysis

The solid residue collected at each operating condition was analyzed by Spectrum One FT-IR spectrophotometer (Perkin-Elmer, Ltd). FTIR analysis determined the structure of the char after the subcritical water treatment. FTIR spectra of the samples were recorded on the FTIR-Spectrum One with the KBr pellet technique. EPFB residue is mixed with laboratory grade KBr, grounded and pelletized with a hydraulic press. Pellet was tested through infrared spectrum in a range of 4000 to 370 $\text{cm}^{-1}$ , with a resolution of 4 $\text{cm}^{-1}$ .

### 2.3.3 GC-MS Spectroscopy

GC-MS spectroscopy equipped with capillary column and selective detector (MSD) analyzed liquid product obtained through experiments. A calibrated Agilent 6890 series GC-MS equipped with a flame ionization detector and a capillary column (SPBTM-5, 30m x 0.32mm x 0.25 $\mu\text{m}$ ) with helium gas as the carrier was used to perform the analysis. Liquid product of 100  $\mu\text{l}$  was pipetted out each from the bottom and upper layer and top up to 10 mL with methanol as diluents in a measuring cylinder. The mixture was shaken to ensure complete mixing. Next, it was filtered into a GC vial and was ready for testing. The GC oven would be kept at 180 $^{\circ}\text{C}$  for 2 minutes, ramped at 4 $^{\circ}\text{C}/\text{min}$  up to 200 $^{\circ}\text{C}$  for 10 minutes.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of catalyst types

Basic catalysts significantly degraded EPFB compared to non-catalytic run in all three parameters discussed in figure 2. Solid conversion jumped from 36.4 %, without catalyst, to 72.4 % in  $\text{K}_2\text{CO}_3$  solution. Similar trend was realized in liquid yield and lignin degradation. Results obtained from NaOH, KOH treatments were within the said extremes and pretty similar to each other.  $\text{K}_2\text{CO}_3 > \text{KOH} > \text{NaOH}$  was the catalyst reactivity order for EPFB degradation proved through these experiments. This may inform about superiority of carbonates in EPFB degradation than to hydroxides which may be due to conversion of  $\text{K}_2\text{CO}_3$  into bicarbonates as secondary catalyst.



$\text{K}_2\text{CO}_3$  presence in supercritical hydrolysis of glucose at 450-550 $^{\circ}\text{C}$  increased liquid yield proving effectiveness of such catalysts in gasification process (Sinag et al. 2003). Low temperature base catalyzed liquefaction of wood at 280  $^{\circ}\text{C}$  for 15 minutes also confirmed the sequence of our present study:  $\text{K}_2\text{CO}_3 > \text{KOH} > \text{Na}_2\text{CO}_3 > \text{NaOH}$ . This may also support potassium bases are effective than sodium (Selhan et al. 2005).

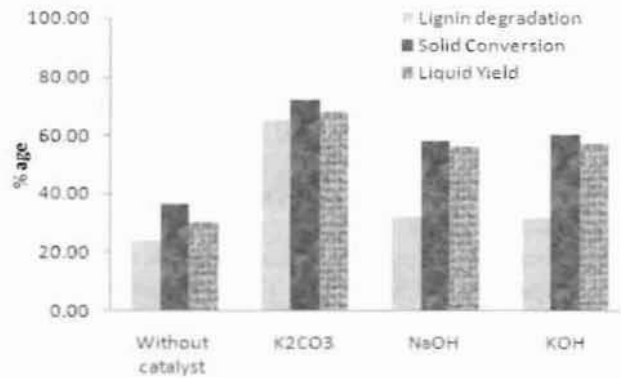


Fig. 2 Effect of various catalysts on amount of liquids in EPFB liquefaction

### 3.2 Effect of $\text{K}_2\text{CO}_3$ concentration

EPFB liquefaction was further analyzed with various concentration of  $\text{K}_2\text{CO}_3$  solution at 270 $^{\circ}\text{C}$ , 5gram/25 ml water ratio.  $\text{K}_2\text{CO}_3$  1.0 M yielded maximum conversion, liquids and lignin degradation. Catalyst concentration supported EPFB breakdown prior to 1.0 M  $\text{K}_2\text{CO}_3$  and discouraged liquid yield beyond 1.0 M.  $\text{K}_2\text{CO}_3$  possibly promoted re-polymerization at high concentrations. Solid conversion and liquid yield were least affected by catalyst concentrations while lignin degradation varied comprehensively (figure 3). Almost 10 % increase in liquids yield was noticed with 40 % extra lignin degradations. This proved almost one fourth effect of lignin on liquid yield as can be seen by original composition of EPFB wherein lignin is about 20 % of total lignocelluloses (Luis et al. 1999).

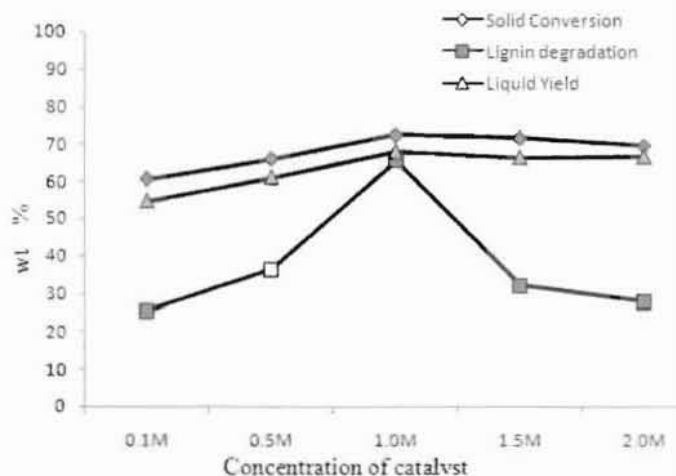


Fig. 3 Effect of  $\text{K}_2\text{CO}_3$  concentration on EPFB conversion and liquid yields

Higher conversion with increasing  $\text{K}_2\text{CO}_3$  concentrations after analyzing effects of various  $\text{K}_2\text{CO}_3$  solutions (0.235 M, 0.47 M, and 0.94 M) on biomass up gradation at 280 $^{\circ}\text{C}$  was reported (Selhan et al. 2006). Furthermore, in our study  $\text{K}_2\text{CO}_3$  solution discouraged conversion beyond 1.0 M  $\text{K}_2\text{CO}_3$  concentrations.

### 3.3 Effect of biomass to water ratio

Higher concentrations of EPFB biomass decreased amount of liquids and lignin degradation. As from figure 4, 68% liquids were achieved with 2:10 EPFB to biomass ratio converting 72% of solid mass at experimental conditions of 270°C, 40 bars, 1.0 M K<sub>2</sub>CO<sub>3</sub> solution. 8:10 EPFB to biomass ratio resulted in the lowest degradation, liquids and solid mass conversion. In a similar study, *cunninghamia lanceolata* was liquefied in water in presence of 280-360°C with different biomass to water ratios (8g, 10g, 12.5 g per 100 ml each) (Yixin et. al. 2003). Results proved high amount of biomass led to low conversion and liquid yield as said in our study.

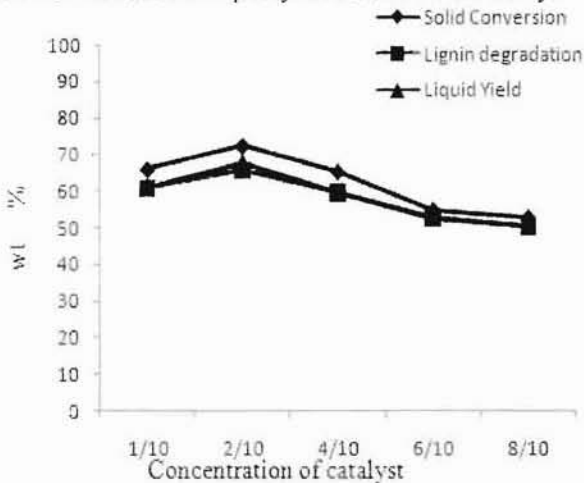


Fig. 4 Effect of EPFB/water ratio on EPFB conversion, lignin degradation and liquid yields

Although smaller biomass to water ratio resulted in better conversion, the use of large amounts of water should be avoided as the high energy inputs incurred high cost.

### 3.4 Liquid oil composition

Liquid products distribution depended strongly on catalyst types and biomass to water ratio as shown in table 1. For 5:25 EPFB to water ratio, maximum ester yield was 86.45 % in 1.0 M NaOH solution while 1.0 M K<sub>2</sub>CO<sub>3</sub> produced 60.08 % phenols. Subcritical hot water system could produce fuel grade bio oil dominated by phenols and esters (see table 1). Similar results have been published in literature (Selhan et. al. 2006).

### 3.5 EPFB and char characterization

Fourier transform infrared (FT-IR) spectroscopy characterized raw EPFB and chars obtained in liquefaction process said above within wave number range 4000 – 370 cm<sup>-1</sup> (figure 5). Various bands in spectrum were identified as O-H (3446.9 cm<sup>-1</sup>), methoxyl (2924.0 cm<sup>-1</sup>), methoxyl (2924.0 cm<sup>-1</sup>), aliphatic C-H bonds (3000-2860 cm<sup>-1</sup>), stretching of aromatic C=C groups (1680-1570 cm<sup>-1</sup>), stretching and bending modes of saturated aliphatic hydrocarbon (2980-2850 and 1400-1300 cm<sup>-1</sup>, respectively) and bending of aromatic C-H groups (900-700 cm<sup>-1</sup>).

Table 1 Percentages of organic groups obtain through GC-Mass analysis of liquid oil under various conditions

Reaction Condition Temperature = 270°C Pressure = 40bar Reaction time =20min	% Area		
	Phenol	Methyl Ester	Benzoic acid
5g EPFB/25ml Water			
Without catalyst	-	26.44	-
K <sub>2</sub> CO <sub>3</sub> 1.0 M	60.08	39.92	-
KOH 1.0 M	18.40	81.6	-
NaOH 1.0 M	6.00	86.45	-
K <sub>2</sub> CO <sub>3</sub> 0.1 M	1.33	2.88	2.89
K <sub>2</sub> CO <sub>3</sub> 0.5 M	1.77	63.48	4.85
K <sub>2</sub> CO <sub>3</sub> 1.0 M	60.08	39.92	-
K <sub>2</sub> CO <sub>3</sub> 1.5 M	34.50	68.50	-
K <sub>2</sub> CO <sub>3</sub> 2.0 M	34.79	65.21	-
K <sub>2</sub> CO <sub>3</sub> 1.0 M			
2.5gEPFB/25ml Water	0.61	94.29	1.72
5gEPFB/25ml Water	60.08	39.92	-
10gEPFB/25ml Water	0.44	41.34	-
15gEPFB/25ml Water	7.63	-	24.28

From figure 5, it is accessed for no catalyst runs chars showed sharp peaks within 1680-1570 cm<sup>-1</sup> band region indicating presence of C=C bonds wherein no such bonds were found in case of catalyzed chars (K<sub>2</sub>CO<sub>3</sub>, KOH, NaOH). This proved the reactive nature of catalyzed chars under said process conditions. However, peaks of O-H bonds (at wave number of 3440-3450cm<sup>-1</sup>) which were still present in catalyzed char residues reflected stability of phenols and alcohols.

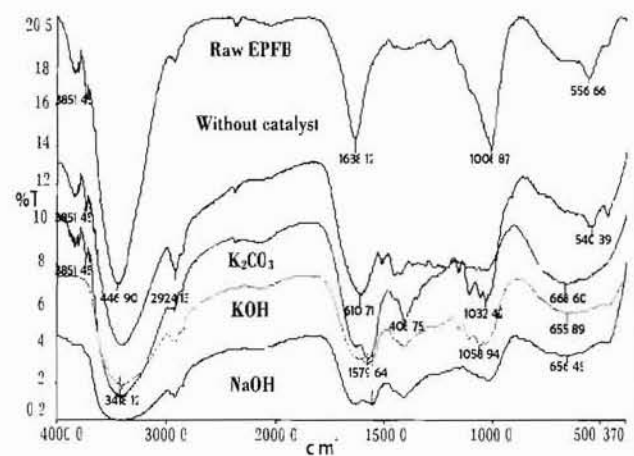


Fig. 5 FTIR analysis of raw EPFB, and residue char on concentration



## CONCLUSION

Among various base catalyst NaOH,  $K_2CO_3$  and KOH screened in this study,  $K_2CO_3$  produced maximum liquids being 68.0 % and degraded 65.62 % lignin under the same operating conditions. Catalysts reactivity order is confirmed as  $K_2CO_3 > KOH > NaOH$  based on liquid yields and solid mass conversion. Furthermore, 1.0 M  $K_2CO_3$  produced the maximum value of solid mass conversion, lignin degradation and liquids when compared with other concentrations of same catalyst. Possibly at high  $K_2CO_3$  concentrations beyond 1.0 M, re-polymerization of fragmented components reduced liquid yield. Higher amounts of EPFB mass also decreased liquid yields and the optimum value obtained through experiments was 2 g/25 ml water. Liquid bio oil thus produced dominantly consisted of phenols and esters according to GC-MS analysis. This confirms superiority of sub critical technique compared to pyrolysis for example wherein a large number of liquid product components daunt oil quality and increase post processing costs.

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