



# Bio-oil production from oil palm biomass via subcritical and supercritical hydrothermal liquefaction



Yi Heng Chan<sup>a</sup>, Suzana Yusup<sup>a,\*</sup>, Armando T. Quitain<sup>b</sup>, Yoshimitsu Uemura<sup>a</sup>, Mitsuru Sasaki<sup>b</sup>

<sup>a</sup> Biomass Processing Lab, Center of Biofuel and Biochemical Research, Mission Oriented Research (Green Technology), Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

<sup>b</sup> Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan

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## ABSTRACT

This paper presents the studies on the liquefaction of three types of oil palm biomass; empty fruit bunch (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) using water at subcritical and supercritical conditions. The effect of temperature (330, 360, 390 °C) and pressure (25, 30, 35 MPa) on bio-oil yields were investigated in the liquefaction process using a Inconel batch reactor. The optimum liquefaction condition of the three types of biomass was found to be at supercritical condition of water i.e. at 390 °C and 25 MPa, with PKS yielding the maximum bio-oil yield of 38.53 wt%, followed by EFB and PMF, with optimum yields of 37.39 wt% and 34.32 wt%, respectively. The chemical compositions of the bio-oils produced at optimum condition were analyzed using GC–MS and phenolic compounds constituted the major portion of the bio-oils, with other minor compounds present such as alcohols, ketones, aromatic hydrocarbons and esters.

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## 1. Introduction

The utilization of biomass has become a significant topic of research recently due to gradual depletion of fossil fuels reserves, energy crisis and the need to reduce the dependency on non-renewable energy sources. Biomass is the main source of carbon in which alternative transportation fuels, fine chemicals, heat and power can be derived from. Besides, the abundance of multiple types of biomass around the globe has provided many prospects for its utilization by developing operable large scale processes to produce renewable energy carriers and chemicals, thus replacing the use of crude-based resources. Bio-oil or bio-crude, in particular, is a liquid product derived from biomass through pyrolysis or other liquefaction processes [1]. It comprises of a mixture of organic compounds and possesses higher energy density compared to biomass raw materials which can be upgraded and utilized in various applications, such as transportation and engine fuels

(biofuels), value-added fine chemicals, food flavorings, fertilizers and agro-chemicals [2].

Bio-oil is conventionally produced from fast pyrolysis processes, where biomass materials are decomposed by heat to produce a mixture of condensable pyrolysis vapor, incondensable gases and char in the absence of oxygen [3]. However, pyrolysis usually requires operation at high temperatures (400 °C and above), near atmospheric pressure and a short vapor residence time ranging from a few milliseconds to seconds to generate primarily bio-oil [4]. Besides, drying of biomass prior to pyrolysis treatment is required and this usually consumes substantial energy due to the high heat of water vaporization [5].

Another recent approach used to convert biomass to bio-oil is through solvolytic liquefaction process. During liquefaction, the complex structure of biomass is decomposed by utilizing a heated and pressurized solvent, thus producing liquid products [6]. The bio-oil is then produced from the raw liquid products using solvent extraction. The production of bio-oil via liquefaction of various feedstocks, such as sewage, livestock manure, algae, domestic and agricultural wastes has been reported in the literature [7,8]. Compared to pyrolysis technology, liquefaction usually occurs at a lower temperature (about 250–400 °C) and higher pressure (5–20 MPa), depending on the solvent used in the liquefaction process. In contrast to pyrolysis process in which biomass decomposes thermolytically via de-polymerization

\* Corresponding author. Tel.: +60 53687642; fax: +60 53688204.

E-mail addresses: [kelvinyiheng@gmail.com](mailto:kelvinyiheng@gmail.com) (Y.H. Chan), [drsuzana\\_yusuf@petronas.com.my](mailto:drsuzana_yusuf@petronas.com.my) (S. Yusup), [quitain@kumamoto-u.ac.jp](mailto:quitain@kumamoto-u.ac.jp) (A.T. Quitain), [yoshimitsu.uemura@petronas.com.my](mailto:yoshimitsu.uemura@petronas.com.my) (Y. Uemura), [msasaki@kumamoto-u.ac.jp](mailto:msasaki@kumamoto-u.ac.jp) (M. Sasaki).

**Table 1**  
Properties of oil palm biomass (dry basis).

Biomass	Structural analysis (%)				Ultimate analysis (%)					Higher heating value (MJ/kg)
	Hemicellulose	Cellulose	Lignin	Extractives and ash*	C	H	N	S	O <sup>a</sup>	
EFB	26.9	26.6	18.6	27.9	43.62	4.03	1.96	0.17	50.22	16.3
PMF	22.2	23.1	30.6	24.1	46.29	4.67	1.42	0.24	47.37	16.5
PKS	22.9	24.5	33.5	19.1	47.77	4.06	0.46	0.16	47.55	17.5

<sup>a</sup> Calculated by difference.

and cracking in an inert condition, liquefaction produces bio-oil from the solvolytic break-down of biomass structure through hydrolysis and hydrogenation reactions, thus leading to different product properties (such as yield and composition of products, energy density, thermal and storage stabilities) [9]. Liquefaction can also convert biomass with high moisture content, hence eliminating the need of drying of biomass feedstock and often results in higher bio-oil yield compared to pyrolysis process, which produces more solid char [9]. Aside from bio-oil and solid char, liquefaction processes also produce carbon-containing aqueous by-products (which contained dissolved organics, sugars and acids) and gaseous by-products (CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>, and other light hydrocarbons) [9]. In addition, the use of solvent in liquefaction process dilutes the concentration of products. This prevents the cross-linking and re-combination reactions which usually occur in the case of slow pyrolysis and gasification at lower temperature and lead to the formation of tar and char [10,11]. Besides, use of solvent in liquefaction processes require lower operating temperature compared to pyrolysis and gasification, hence incur less operating cost due to less energy consumption [10,11].

Subcritical and supercritical liquefaction has gained attention as one of the promising thermochemical conversion processes of biomass into bio-oil. In particular, subcritical liquefaction occurs at temperature range of boiling point to critical point or near to critical point of the solvent (for water, liquefaction of biomass usually occurs at 200 °C and above [12]) whereas supercritical liquefaction utilizes a fluid formed at conditions above the critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) of the particular solvent [13,14]. Due to lower critical parameters of some organic solvents compared to that of water, solvents such as methanol, ethanol, acetone and phenol have been frequently utilized in previous liquefaction studies [10,14,15].

As water is naturally contained in biomass, subcritical and supercritical liquefaction using water is used in this study rather than organic solvents. In addition, compared to organic solvents, water is a green solvent, relatively cheap and abundant, non-flammable and non-toxic, which makes it a good solvent for liquefaction of biomass and extraction of bio-oil components at subcritical and supercritical hydrothermal conditions, as well as a safer operation in larger production scale in the future. Subcritical water has low dielectric constant, weak hydrogen bond and high isothermal compressibility compared to ambient liquid water. Hence it has been utilized in various synthesis and degradation reactions and it is suitable to be employed in biomass degradation and decomposition to form gas, liquid and solid products [14]. Supercritical water possesses the unique properties in between that of liquid water (liquid-like densities) and gaseous water (high diffusivities and compressibilities) which will enhance the solubility, extraction and separation of organic compounds [16]. As water is approaching its critical state and beyond, the dielectric constant decreases, enabling many organic compounds to be soluble in water, up to total miscibility [12]. The ionic product of subcritical water is relatively high ( $10^{-12}$  compared to  $10^{-14}$  for ambient water). As such, higher concentrations of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions promote ionic reactions which are usually acid or base-catalyzed [17].

Beyond the critical point of water, the ionic product decreases, leading to more radical reactions in the reaction medium. As such, subcritical and supercritical water not only play the role as a medium in which liquefaction occurs, they also act as a catalyst and reactant for the decomposition and hydrolysis of biomass, making it a suitable candidate to liquefy lignocellulosic biomass for production of bio-oil.

As Malaysia is a major producer of palm oil in the world, it contributes to the generation of oil palm biomass wastes in staggering amounts, approximately 86.9 Mt/year as in 2010 [18]. As such, they can be utilized as feedstocks for conversion to bio-oil. In this work, EFB, PMF and PKS are converted to bio-oil via subcritical and supercritical hydrothermal liquefaction at various temperatures and pressures. The bio-oils produced at optimum liquefaction conditions are analyzed for their chemical compositions and the findings are discussed.

## 2. Materials and methods

### 2.1. Biomass pre-treatment and characterization

Fresh empty fruit bunch (EFB), palm mesocarp fiber (PMF) and palm kernel shell (PKS) obtained from FELCRA Nasaruddin Oil Palm Mill, Bota, Perak, Malaysia were washed with water thoroughly to remove sand particles and impurities. They were then manually chopped into smaller pieces, dried in the oven at 80 °C for 48 h, grinded with a FRITSCH Cutting Mill and sieved to a particle size of <710 μm before being used as feedstocks in the experiments.

The feedstocks were characterized for their structural and elemental compositions, higher heating value (HHV) and thermal degradation behavior by differential thermogravimetric analysis (DTG). Biomass samples were sent to Forest Research Institute Malaysia (FRIM) for analysis on the structural contents which consist of hemicelluloses, cellulose and lignin, while the remaining components were assumed to be extractives and ash, as reported in the literature pertaining to characterization of lignocellulosic biomass [19,20]. Elemental compositions and higher heating values were determined using a LECO 932 CHNS Analyzer and IKA C5000 Bomb Calorimeter, respectively. Table 1 shows the properties of the oil palm biomass used in this study. Differential thermogravimetric analysis (DTG) were conducted using EXSTAR 6000 TG/DTA6300 from 35 °C to 500 °C with heating rate of 20 K/min using nitrogen as carrier gas.

### 2.2. Subcritical and supercritical hydrothermal liquefaction

EFB, PMF and PKS were subjected to subcritical and supercritical hydrothermal liquefaction conditions, as shown in Table 2. As the liquefaction experiments involved subcritical and supercritical water, suitable temperature range of 330–390 °C was chosen as high temperatures (above 400 °C) will increase the dominance of gasification reaction [6]. The pressure range of 25–35 MPa was chosen since it is above the critical pressure of water (22.1 MPa) to ensure that water is in the subcritical and supercritical state [21]. Prior to the experiments, the densities and dielectric constants of water at the experimental conditions were determined

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