Influence of temperature on liquid products yield of oil palm shell via subcritical water liquefaction in the presence of alkali catalyst

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ARTICLE INFO

ABSTRACT

Oil palm shell (OPS) was converted to various liquid products through subcritical water liquefaction using a high-pressure autoclave reactor with and without the presence of K_2CO_3, Na_2CO_3, or NaOH as alkali catalyst at a temperature ranging from 483 to 603 K. Liquid products obtained were sub-classified to bio-oil and water soluble. In the absence of any catalyst, conversion of solid OPS increased from 44.5% to 65.8% as temperature rises from 483 to 603 K which is equivalent to the amount of hemicellulose and cellulose available in the OPS used (it has complete consistency with thermogravimetric analyses). However, with the addition of alkali catalyst, solid conversion and liquid product yield increased significantly. The use of 10% K_2CO_3 and 10% Na_2CO_3 gave almost similar results while the addition of 10% NaOH resulted to the highest solid conversion and liquid product at 84% and 53.4% respectively. In addition, the use of 10% NaOH also resulted to significantly lower gaseous product as compared to those with either other catalysts or without any catalyst at similar condition. The liquid product yield obtained is two times more than those obtained via the use of pure water subcritical liquefaction.

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1. Introduction

Today, the world society is confronting to serious and strategic problems such as environmental pollution, global climate change, rising energy prices, depletion of limited fossil fuel resources, and dependency on limited oil exported countries because of increasing fossil energy consumption. Therefore, it is necessary to look for and develop the future alternative fuels' resources due to the environmental problems.

There are various alternative energy resources available at present, encompassing hydro, biomass, wind, solar, hydrogen, and nuclear energy. Among these, biomass, which is an important resource convertible in energy, has been the subject of interest recently. In particular, forestry wasted and agriculture residues are the oldest and most useful resources of energy from which humans acquired energy traditionally. Besides that, owing to its wide availability in many parts of the world, biomass is popular internationally. Using indigenous sources of biomass for energy supply can avoid monopoly of markets by certain countries. Furthermore, the use of biomass as a substitute for fossil fuels can reduce the carbon content in the atmosphere as carbon dioxide is absorbed by plants via photosynthesis during their growth [1].

Thus, biomass is currently the fourth largest source of energy in the world. At present, this energy source supplies about 1185.84 million

TOEs (Mtoe), consisting around 12.9% of the world's annual energy consumption. This portion is higher than that contributed by coal but is comparable to that contributed by gas and electricity [2]. Biomass is constituted mainly of forestry waste, energy crops, aquatic and waste biomass, and agricultural residues [3].

Thermochemical conversion using subcritical to supercritical liquefaction is one of the methods to convert biomass into liquid products (LPs). Thus, some researchers have recently liquefied some lignocelluloses (various types of biomass) using subcritical to supercritical fluid with or without catalysts [4]. The methods used include rapid hydrolysis of cellulose in subcritical and supercritical water (SCW) without the addition of any catalyst, conversion of lignocelluloses into bioenergy and chemicals using supercritical fluid technology, and catalytic hydrothermal treatment of woody biomass in the presence of K_2CO_3 with different concentrations and biomass/water ratio [5–8].

In the work of Ehara and Saka, ether and ester linkages of woody biomass were instantly hydrolyzed in subcritical or supercritical water [9]. Furthermore, Qianand Cheng have investigated the effects of temperature and reaction time on product distribution and yields of chemical products by subjecting switchgrass to subcritical water [10,11]. Moreover, Qian also showed that the main liquefied product was significantly influenced by the process condition in direct liquefaction of woody biomass by water with Na_2CO_3 as a catalyst in an autoclave [11]. Wahyudiono et al. demonstrated that with increasing reaction time of lignin degradation in near supercritical water process, the amount of higher molecular weight fractions decreased while the amount of lower molecular weight fractions increased [12].

Among all conversion methods, thermochemical liquefaction in subcritical water has enticed many scientists' attentions recently because this process could eliminate the sample pre-treatment step and reduce reaction time while achieving high liquefaction efficiency as in the conventional process such as pyrolysis [13]. Subcritical water is defined as liquid water at temperatures between the boiling point and the near critical point (373–647 K), which is appropriately used as a medium for organic chemistry reactions [14].

Subcritical water exhibits properties that are very different from those of ambient liquid water. For instance, subcritical water has a lower dielectric constant, weaker hydrogen bonds and a higher isothermal compressibility than ambient liquid water. These properties make subcritical water a very promising reaction medium for conversion of biomass such as lignocellulosic materials. It has the ability to break the rigid structure of lignocelluloses and consequently, decompose the lignocellulosic materials into smaller components by hydrolysis and further reactions [14,15]. Thus, subcritical water liquefaction has been widely employed for an efficient production of liquid bio-oil and valuable chemicals from wasted biomass.

Actively promoting agricultural activities, Malaysia is a country abounding in biomass wastes. Being one of the main palm oil producing and exporting countries in the world, oil palm is treated as one of its most important agriculture crops. In 2009, 4.88 million ha of land in Malaysia was covered by oil palm cultivation; producing 90.40 million tons of fresh fruit bunches (FFB). The amount of oil palm biomass produced by these oil palm plantations in that year was estimated to be about 37.0 million tons, consisting of 5.5% of shell [16,17]. It has been proven that biomass sources can become an economical source of renewable energy. Besides that, it is also undisputed that indiscriminate disposal of these wastes would result in serious environmental problems. Thus, developing new technologies to convert oil palm biomass into energy sources (liquid or gas) becomes an attractive field of research.

In our previous study, we have reported the conversion of oil palm fruit press fiber (FPF) to biofuel using subcritical water liquefaction and using supercritical organic solvent [3,4]. However, in this work, this article underlines the study of alkali catalysts' effects on the efficiency of using subcritical water to decompose oil palm shell (OPS) into various liquid and residual solid waste products. The decomposition of OPS was carried out in a high-pressure batch reactor with and without the presence of catalyst such as K_2CO_3, Na_2CO_3, and NaOH.

2. Methods

The OPS was taken from one of the oil palm mills in Malaysia. The air-dried OPS were grounded and screened. Only the portion with particles size between710 and 1000 μm was used. Then, the OPS elements were analyzed. The structural analysis was carried out according to the Technical Association of the Pulp and Paper Industry standard (TAPPI's) test methods whereas the element analysis (e.g. CHNS/O) was implemented with CHNS/O analyzer (Series Π CHNS/O Analyzer 2400). The results are tabulated in Table 1. This table shows that oil palm shell (OPS) contain relatively high extractive matter content. The elemental compositions of the liquid products (WS and Bio-Oil) were also analyzed in the same manner as the raw OPS. In addition, in order to explicate the effect of subcritical water treatments on decomposition of hemicellulose, cellulose, and lignin of OPS, the solid residual of runs was also analyzed in the Thermogravimetric Analyzer (TA Instrument,

SDT Q600). Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) profiles of pristine OPS and solid residual of runs were obtained by heating under nitrogen gas with heating flow rate of 20 °C/min.

Water in the presence and absence of 10% catalyst (i.e. potassium carbonate, sodium carbonate, and sodium hydroxide) was used respectively in the experiments. For each run, the reactor was heated from room temperature to the desired temperature. All the subcritical experimental runs were performed using 10 g of air dried OPS by varying temperatures between 483 and 603 K. Experiments were conducted in a 450 ml high-pressure autoclave reactor (supplied by Buchi Glas Uster, Model "Limbo Li" Switzerland).

In a typical run, 10 g of air dried OPS powder (710 to 1000 μm) and 100 ml of water or solution with a desired amount of catalyst were loaded into the autoclave reactor which was then plugged with ten screw bolts. Subsequently, the reactor was purged with nitrogen gas (purification) to remove any residual air and to increase the reactor pressure to 10 bars. The heat supply to the reactor was provided by an external jacket heater, in which the power was adjusted to give an approximate heating time of 45 min. The temperature of the high-pressure vessel was measured using an iron-constantan thermocouple and the temperature was controlled at the desired level for 60 min [18]. After each run, the gas was vented. The gas products were not analyzed in this work as our main interest was the liquid products. Moreover, from a thermodynamics point-of-view, gasification process normally leads to similar gas compositions containing CH_4, CO_2, CO and H_2 [19]. The solid and LPs were separated from the autoclave into a beaker. Finally, the oil and solid residues were removed from the autoclave by washing them with used solvents. The liquid soluble product from the reactor consists of polar or aqueous phase containing organo-oxygen compounds with low molecular weight, and a non-polar or non-aqueous phase containing insoluble organics (mainly aromatics and organic compounds) with high molecular weight. The former is called water soluble whereas the latter is called bio-oil, heavy oil. It is noteworthy that the latter have limited solubility in diethyl ether, diethyl acetate, and acetone. Based on the polarity of solvents, diethyl ether, diethyl acetate, and acetone were used as the solvents to extract the components of liquid soluble products. The products taken out from the reactor had been filtered with filter paper under vacuum for 10 min to separate the solid and LPs. During filtration, 50 ml of diethyl ether solvent was used to wash the solid products. The filtrate was then extracted with diethyl ether by using liquid–liquid extraction procedure in a separatory funnel. The two portions obtained through this separation are called water-soluble and diethyl ether soluble products. Water and diethyl ether were removed from the two portions separately using rotary evaporator system (Büchi Rotavapor R-215) under reduced pressure, and the remaining fractions were weighed and designated as water solution (WS) and diethyl ether soluble (DES) products, respectively. In the same manner, the solid residue and water solution were also extracted using diethyl acetate. After removal of diethyl acetate from water using a rotary evaporator under reduced pressure, the fractions were weighed and designated as diethyl acetate soluble (DAS) and water soluble (WS) products, respectively.

Likewise, the solid residue was also washed using acetone. After removal of acetone using a rotary evaporator under reduced pressure, the fractions were weighed and designated as acetone soluble (AS) products. Finally, the acetone insoluble fraction was dried until constant weight was recorded in an oven at 378 K, called the solid residue including unconverted OPS.

Table 1
Chemical and elemental analysis of oil palm shell (wt.% of dry basis).

Cellulose	Hemicelluloses	Lignin	Extractives[a]	Moisture	Carbon	Hydrogen	Oxygen	Nitrogen
39.7	21.8	32.5	6.0	7.5	50.01	7.66	29.02	13.31

[a] Soxhelet extractives were obtained by using ethanol–toluene (2/1, v/v).