

Fractionation of Bio-oil By Supercritical CO₂

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ABSTRACT

Interest in biomass as a clean source of fuel, chemicals and materials is growing fast. Biomass is considered as a relatively clean fuel as it decreases or even eliminates net CO₂ emission and has low sulphur and NO_x content in comparison with fossil fuels. The bio-oil under study contained 45% of water and it forms azeotrope with polar organic compounds. The work has been carried out to isolate the organic fraction of the bio-oil by supercritical CO₂. The supercritical CO₂ fractions are characterised by CHNS, GC-FID, GC/MS, and ¹H-NMR. The supercritical CO₂ fractions are enriched with furanoids, pyranoids and benzenoids. The supercritical CO₂ is an advanced method for selective extraction of valuable chemicals from bio-oil with trace amount (<2.5%) of water.

INTRODUCTION

In future bio-oil produced from biomass will be the most potentially promising alternative fuel for the transport sectors owing its ecological advantage. These renewable energy sources become quickly popularized due to their lack of environmental risks and pollution. Biomass materials are natural high molecular substances composed of carbon, hydrogen, oxygen and nitrogen. Biomass such as wood waste, sawdust and agriculture waste can be easily acquired in all parts of country. It has been identified as a sustainable source of renewable energy [1] Biomass can reduce the dependency on fossil fuels and mitigate global warming somewhat by reducing CO₂ emissions. In addition, some forms of biomass can be used as alternative materials in chemical feedstock [2]. Although may having different types of method of production of bio-oil from different types of biomass, it has been found that “Fast Pyrolysis” with its very short residence time can obtain a high yield of bio-oil [3]. Particularly fluidized bed process has advantage in that it can promote heat transfer from heat sources to raw materials thorough a mixing effect [4]. So the fast pyrolysis using fluidized bed process is popularly used in industrial scale of production. Pyrolysis was the thermochemical process that converted organic materials in to usable fuels. Pyrolysis produced energy fuels with fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method most capable of completing with and eventually replacing non-renewable fossils fuel resources [5]. The wheat-sawdust bio-oil contained high percentage of water in compared to the bio-oil reported from other biomass [6-8]. The complexity of the bio-oil

composition provides the potential for obtaining chemicals. The challenge is the separation of products for chemicals and liquid fuel in an economical way from the crude bio-oil. It is observed that the crude bio-oil is polymerised within few weeks at room temperature due to high percentage of oxygen along with water. So the removal of water from the bio-oil is essential for storage and calorific value of the liquid fuel.

The supercritical CO₂ extraction is commonly used for extraction of natural material because of the non-toxic, non-flammable characteristics of CO₂ and its availability in high purity with low cost. Reverchon *et al.* reviewed, the numerous works carried on the application of supercritical CO₂ in food processing, pharmaceuticals and nutraceuticals [9]. King *et al.* studied the mutual solubilities of water with supercritical and liquid CO₂ and they observed the solubility of water with CO₂ is ~3.0 mole fraction at 25 MPa pressure [10]. This is an advantage to select the fractionation of bio-oil with CO₂ to get moisture free extract is an attractive alternative. There is no literature available on separation of organic components from bio-oil by using supercritical CO₂.

MATERIALS AND METHODS

In the present study the bio-oil, which produced from wheat-sawdust biomass by fast pyrolysis process is collected from Advanced Biorefinery, Canada. The extraction and analysis are carried out 2-3 times and data presented the average of these readings.

The crude bio-oil is fractionated by supercritical CO₂ in the following methodology. The laboratory design supercritical CO₂ unit of Thar Technologies is used for fractionation study and CO₂ used in the experiment is 99.9% pure supplied by Praxair, Canada. Bio-oil (25 g) is mixed with clean 2 mm glass beads and filled the extractor to half of the volume. The supercritical CO₂ fractionation is carried out at 45 °C with CO₂ flow rate of 30 g/min. The first fraction collected after 2 hours time interval. Again the raffinate bio-oil in the reactor is extracted for another 2 hours to get the second fraction. Similarly all total four fractions are collected. The first three fractions are collected at 25 MPa pressure. The fourth fraction is collected at 30 MPa pressure and other parameters are same as mentioned above.

The calorific value and P^H of supercritical CO₂ fractions are determined by Bomb calorimeter and P^H meter respectively. The chemical characterisation are carried by CHNS, GC-FID, GC/MS and ¹H-NMR analysis

The calorific value is determined in a static bomb calorimeter, a sealed Parr 1108, following the procedure described by Hubbard *et al.* [11].

The common organic elements viz. C, H, N and S are analysed in Vario Elementar CHNS analyzer. The sample (5.0 mg) is taken in a tin capsule assortment for percentage composition of C, H, N and S analysis and the percentage O is determined by means of difference.

GC analysis is carried out on a Varian CP-3800 Gas Chromatograph equipped with a flame ionization detector (FID) and a 30 m x 0.25 mm WCOT column coated with 0.25 μm film thickness of 5% diphenyl dimethyl siloxane supplied by J &W (DB-5). Helium is used as the

carrier gas at a flow rate of 1.2 mL/ min at a column pressure of 22 KPa. 0.2 µl of each sample is injected into the injection port of the GC using a split ratio of 50:1. Compound separation is achieved following a linear temperature program of 50°-250 °C (5 °C/min), 250 °C (20 min), so the total run time is 1 hour. Percentage composition is calculated using peak normalization method assuming equal detector response. The GC/MS analysis is carried out on a Varian Saturn 2200 GC/MS fitted with the same column and temperature programmed as above. MS parameters: ionization voltage (EI) 70 eV, peak width 2 sec, mass range 40-500 amu and detector voltage 1.5 volts. Peak identification is carried out by comparison of the mass spectra with mass spectra available on NIST-I and NIST-II libraries. The compound identification is finally confirmed by comparison of their relative retention indices (RRI) with literature values [12,13]. The RRI of the peaks is calculated by standard sample mixture of normal saturated hydrocarbons C-8 to C-22 is injected into the GC column under the same conditions of sample analysis [14].

¹H-NMR is recorded on DPX-500 Bruker UltraShield™ at 500 MHz at 25 °C. For bio-oil, 0.2 g of sample is dissolved in CD₃OD and for supercritical CO₂ fractions; 0.2 g of sample is dissolved in CDCl₃ for spectral analysis.

RESULTS

The complexity of the bio-oil composition provides the potential for obtaining chemicals. The challenge is the separation of products for chemicals and liquid fuel in an economical way from the crude bio-oil. It is observed that the crude bio-oil is polymerised within few weeks at room temperature due to high percentage of oxygen along with water. So the removal of water from the bio-oil is essential for storage and calorific value of the liquid fuel. The yields of the supercritical CO₂ extracts are 5.0 g, 3.7 g, 1.5 g and 1.2 g for first to fourth fraction respectively.

The ultimate analyses, moisture content, calorific value and P^H of the bio-oil and supercritical CO₂ fractions are presented in Table 1. The bio-oil contained very low percentage of carbon and very high percentage of oxygen. The empirical formulae suggested that the bio-oil contained more oxygen in compared to the biomass, so it is not suitable for direct application as fuel may be due to the high percentage of water. In the process of prevalent dehydration of polysaccharides and lignin, water arises in considerable amounts [15]. In considering the empirical formulae the supercritical CO₂ fractions are superior in quality with less percentage of oxygen. It is observed that the calorific value of the supercritical CO₂ fractions of the bio-oil are higher in compared to the biomass. The crude bio-oil calorific value is very low and could not determine in bomb calorimeter in most of the trial due to the high percentage of water. Similarly, the ultimate analyses of CO₂ fractions indicated that the carbon percentage is increased with decreased the percentage of oxygen as presented in empirical formulae. So, the supercritical CO₂ fractions are contained very few percentage of moisture (~2.5%) along with high percentage of carbon.

Table 1: Ultimate analysis, calorific value and P^H

Samples	C (%)	H (%)	N (%)	S (%)	O* (%)	H/C molar ratio	O/C molar ratio	empirical formulae	moisture content (%)	calorific value (MJ/Kg)	P ^H
Biomass	47.6	6.2	0.07	0.05	46.0	1.6	0.7	CH _{1.6} O _{0.7} N _{0.001}	5.0	19.1	-
Bio-oil	17.9	10.0	0.08	0.02	71.9	6.7	3.0	CH _{6.7} O _{3.0} N _{0.004}	46.8	-	2.7
Sc-CO ₂ fraction (first)	55.5	7.7	0.14	0.05	36.6	1.7	0.5	CH _{1.7} O _{0.5} N _{0.002}	2.5	30.1	5.0
Sc-CO ₂ fraction (second)	75.4	11.6	0.01	0.04	12.9	1.8	0.1	CH _{1.8} O _{0.1} N _{na}	0.1	44.2	4.3
Sc-CO ₂ fraction (third)	77.9	11.9	0.02	0.01	10.1	1.8	0.1	CH _{1.8} O _{0.1} N _{na}	0.2	42.5	4.1
Sc-CO ₂ fraction (last)	78.8	12.2	0.02	0.01	8.9	1.9	0.08	CH _{1.8} O _{0.08} N _{na}	0.5	36.0	3.9

* determined by difference of C, H, N and S, na<0.0001

In GC-FID and GC/MS analysis revealed that the first fraction is rich with furanoids, pyranoids and benzenoids with very few percentages of long chain fatty acids and waxy components. The empirical formulae suggested that the first fraction is enriched with oxygen due to the improved percentage of polar compounds. Similarly later fractions are enriched with hexadecanoic acid and waxy components. So, supercritical CO₂ selectively separated the valuable chemicals from the crude bio-oil. The chemical compositions of all four fractions are presented in Table 2.

Table 2: Yield and chemical classes of bio-oil and bio-oil fractions

Chemical classes	25 MPa (first)	25 MPa (second)	25 MPa (third)	30 MPa
Yield (%)	20	15	5	6
Hydrocarbons	13.2	2.6	2.7	0.5
Low molecular wt. fatty acids/ esters	11.8	8.9	7.3	4.4
furanoids	9.9	4.2	4.1	0.8
pyranoids	9.0	1.8	1.3	1.0
Benzenoid hydrocarbons	5.5	9.4	9.2	9.7
Oxygenated benzenoids	39.3	20.7	19.8	15.8
Low molecular wt. alcohols/ aldehydes/ ketones	2.9	2.1	1.8	1.1
Hexadecanoic acid	1.6	35.6	38.0	44.0
High molecular wt alcohols	0.5	3.8	3.9	5.3
High molecular wt. waxy components	-	1.1	1.4	3.0

The hydrogen distribution of ¹H-NMR of crude bio-oil and supercritical CO₂ fractions of bio-oil are presented in Table 3. In case of supercritical CO₂ fractions, the decrease of aromatic character from first to fourth fraction and reverse in aliphatic character. So the initial fractions are enriched with benzenoids and valuable oxygenated compounds. The bio-oil is inferior in quality due to water content. Similarly the analysis of bio-oil by ¹H-NMR of pyrolysis and steam pyrolysis of cottonseed cake was reported by Ozbay et al. [16].

Table 3: ¹H-NMR of bio-oil supercritical CO₂ fractions (percentage of total hydrogen)

Chemical shift (ppm)	Type of hydrogen	Bio-oil*	25 MPa (first)	25 MPa (second)	25 MPa (third)	30 MPa
6.5-9.0	aromatic	0.5	7.8	0.5	0.3	0.2
5.0-6.5	phenolic (OH) or olefinic proton	2.9	12.8	10.3	10.7	8.0
3.4-4.5	ring join methylene (Ar-CH ₂ -Ar)	9.0	21.3	4.8	4.5	3.0
2.0-3.3	CH ₃ , CH ₂ and CH to an aromatic ring	16.9	40.0	22.3	21.4	18.9
1.6-2.0	CH ₂ and CH β to an aromatic ring	6.0	7.9	6.1	6.0	5.4
1.0-1.6	β-CH ₃ , CH ₂ and CH γ or further from an aromatic ring	11.3	8.9	46.1	46.7	50.3
0.5-1.0	CH ₃ γ or further from an aromatic ring	3.3	1.1	9.8	10.2	11.5

*Bio-oil contained water peak at 5.1 ppm, which is not taken into account

CONCLUSION

The crude bio-oil is not found suitable as fuel due to high percentage of water content. The supercritical CO₂ effectively separated the water from the crude bio-oil and the resulted fractionated bio-oil has high calorific value. The first fraction contained improved percentage of furanoids, pyranoids and benzenoids with very few percentages of high molecular weight fatty acid and waxy components. The calorific value of the first fraction is less might be higher percentage of these oxygenated components. But later fractions are contained improved percentage of fatty acids and alcohols with higher calorific value. The commercial applications of the bio-oil exist in the field of production of food aromas [15]. So the bio-oil is considered as a source of valuable chemicals and food flavours. The supercritical CO₂ first fraction is enriched with valuable chemicals and may be considered for high value chemicals. The supercritical CO₂ extraction process comes under green technology and may be implemented for value addition of bio-oil. This is the first report on selective separation of bio-oil by using supercritical CO₂.

REFERENCES:

- [1] KLASS, D.L., Biomass for renewable energy, fuels and chemicals, Academic Press, New York **1998**, p. 495
- [2] BRIDGWATER, A., A guide to fast pyrolysis of biomass for fuels and chemicals, PyNe Newsletter Guide, Aston University, UK, 1st March, **1999**.
- [3] ZANZI, R., SJO, K. STRO, M., BJO RNBOM E., Biomass Bioenerg, Vol. 23, **2002**, p. 357
- [4] LEE, S.H., LEE, J.G., CHOI, Y.C., KIM J.H., J. Ind. Eng. Chem, Vol. 12, **2006**, p. 39
- [5] FISHER T, HAJALIGOL M, WAYMACK B, KELLOGG D, J. Analytical and Applied Pyrolysis, Vol. 62, **2002**, p. 331
- [6] MULLEN, C.A., BOATENG, A.A., Energy Fuel, Vol. 22, **2008**, p. 2104.
- [7] SENSOZ, S., ANGIN, D, Bioresour.Tech, Vol. 99, **2008**, p. 5498.
- [8] MEIRE, D., FAIX, O., Bioresour. Tech, Vol. 68, **1999**, p. 71.
- [9] REVERCHON, E., MARCO, I.D., J. Supercrit. Fluid, Vol.38, **2006**, p.146.
- [10] KING, M.B., MUBARAK, A., KIM, J.D., BOTT, T.R., J. Supercrit. Fluid, Vol.5, **1992**, p.296.
- [11] HUBBARD, W., SCOTT, D., WADDINGTON, G., In: Rossini (Eds.), Experimental Thermochemistry. I. Interscience publisher, **1956**, chapter 5.

- [12] YUPING, Z., JIMING, L., YAN, X., HUI, D., WENLAI, F., GUANGAO, Z., *Chin. J. Chromatogr*, Vol. 26, **2008**, p. 212.
- [13] VICHI, S., SANTINI, C., NATALI, N., CLAUDIO, R., LOPEZ-TAMAMES, E., BUXADERAS, S. *Food Chem*, Vol.102, **2007**, p. 1260.
- [14] ROUT, P.K., NAIK, S.N., RAO, Y.R., JADEJA, G., MAHESHWARI, R.C., *J. Supercrit. Fluid*, Vol. 42, **2007**, p. 334.
- [15] MEIRE, D., FAIX, O., *Bioresour. Tech*, Vol. 68, **1999**, p. 71.
- [16] OZBAY, N., PUTUN, A.E., PUTUN, E., *J. Anal. Appl. Pyrolysis*, Vol.60, **2001**, p. 89.