

## Renewable Source of Phenols from Eucalyptus Wood for Enhanced Oil Recovery

Wan Sulaiman, W.R.<sup>1,2,\*</sup>, Euy Soo Lee<sup>1</sup>

<sup>1</sup>Dongguk University, Seoul, South Korea, <sup>2</sup>Universiti Teknologi Malaysia, Johor, Malaysia  
(wanrosli.utm@gmail.com\*)

### Introduction

In general, enhanced oil recovery (EOR) is an oil recovery process involving the injection of materials into the reservoir for the purpose of increasing the amount of crude oil that can be extracted from an oil field. Chemical flooding of oil reservoirs is one of the most successful methods for enhance oil recovery from depleted reservoirs at low pressures. However, this method is not widely applied due to the high cost of chemicals. The cost of these chemicals can be reduced significantly by replacing the petroleum-based phenols in EOR with sources from renewable phenolic compounds extracted from Eucalyptus wood or well known as Pine wood via pyrolysis process. Our preliminary study shows that pyrolysis oil from Eucalytus wood contained high volume of phenolic compounds. Pyrolysis technique is described as thermal degradation of materials in absence of oxygen [1] and is widely used in the production of value added products, fuels and chemicals from biomass waste. Three products are usually obtained from pyrolysis process: gas, liquid and char. Both the product yield and chemical composition of pyrolysis oil can be varied according to the pyrolysis methods and process conditions [2]. Isolation of chemicals at the industrial scale for example has been performed to recover commodity compounds such as methanol, acetone, acetic acid and mixture of phenols [3]. Hence, this study focuses on the production of pyrolysis oil using pyrolysis technique and treats the oil through liquid-liquid extraction for the recovering of valuable pure phenols, such as phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol and aimed at being a substitute to the conventional petroleum based phenols in the EOR system.

### Experimental

Eucalyptus wood was grinded and sieved to a particle size of 212 – 425  $\mu\text{m}$ . It was then dried in the oven for 24 hours at 100°C prior to pyrolysis process. The Eucalyptus wood particles were then feed into the reactor by a motor driven screw feeder. The experimental system used to produce pyrolysis oil was a fluidized bed pyrolysis unit with silica sand as the bed material. The reactor was constructed of stainless steel with full gas flow and temperature control. The reactor was heated externally. The incoming fluidizing gas was nitrogen and was preheated before entering the reactor. The silica sand in the fluidized bed has a mean size of 256  $\mu\text{m}$  diameter. The biomass particles were transferred into the reactor at a feeding rate of 0.6 kg/hr, which was operated at the temperature of 450°C with a gas residence time less than 1 second. The products obtained from the process were pyrolysis oil, char and

gas. The char was entrained and blown from the fluidized bed in the cyclone while the vapors were passed through a water-cooler condenser to ice-cooled collectors to trap the derived liquid oil. Pyrolysis vapor condensed into liquid and was collected in the liquid collectors.

Fourier Transform Infra-Red (FTIR) spectrophotometer was used to characterize the pyrolysis oil. The functional groups presence in the pyrolysis oil can be determined from the infra-red spectrum. The chemical components of the sample was separated and identified with a Agilent 6890N Network GC system using a 30m x 0.25mm x 0.25 $\mu$ m Agilent DB-WAXETR capillary column. The oven temperature was controlled at 35°C for 1 minute and heated at a rate of 5°C min<sup>-1</sup> until the temperature reached 280°C. Data were acquired with the NBS mass spectra library database. Sample was injected directly into the GC column to minimize loss of the oil components and avoid obstruction of the capillary column.

#### *Liquid-liquid extraction of phenolic compounds from pyrolysis oil*

Liquid-liquid extraction is a method used to separate compounds based on their relative solubility in two different immiscible liquids. The extraction of phenol-rich compounds in pyrolysis oil consisted of five main steps. The pyrolysis oil containing the desired phenols was dissolved in standard solvent then sodium bicarbonate solution was added to extract strong organic acids and highly polar compounds. An aqueous sodium hydroxide solution was added to extract phenols by converting them into water-soluble phenolate ions then phenols were regenerated by acidification of the aqueous layer with sulfuric acid. Lastly, a phenolic-rich fraction was recovered by solvent extraction of the acidic aqueous layer. The experiment was performed at room temperature.

### Results and Discussion

#### *Compositional Analysis*

The pyrolysis oil produced from Eucalyptus wood was characterized by using FTIR. The spectrum recorded after scanning on the FTIR is shown in Figure 1. Table 1 represents the functional group compositional analysis for the pyrolysis oil. The presence of water impurities and other polymeric O-H in the pyrolysis oil was indicated by the absorbance peak of O-H stretching vibration between 3650 - 3100 cm<sup>-1</sup>. The alkanes group was indicated by the absorbance peak of C≡C stretching in between 2200 - 1950 cm<sup>-1</sup>. The absorbance peaks between 1780 - 1640 cm<sup>-1</sup> represented the C=O stretching vibration indicated the presence of ketones and aldehydes. The frequency range of 1680 - 1580 cm<sup>-1</sup> presented alkenes of C=C stretching. The peaks in between 1300 - 950 cm<sup>-1</sup> were indication of the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters due to the C-O stretching and O-H deformation vibrations. Absorbance peaks between 900 - 650 cm<sup>-1</sup> indicated the presence of single, polycyclic and substituted aromatic compounds. Table 2 shows the results of

GCMS analysis of pyrolysis oil. From the results, it shows that the pyrolysis oil contains high fraction of phenolic compounds, up to 56.04 area %. The other compounds in pyrolysis oil comprised of benzoic acids, ketones (cyclopentenone), aldehydes (benzaldehyde) and benzene.

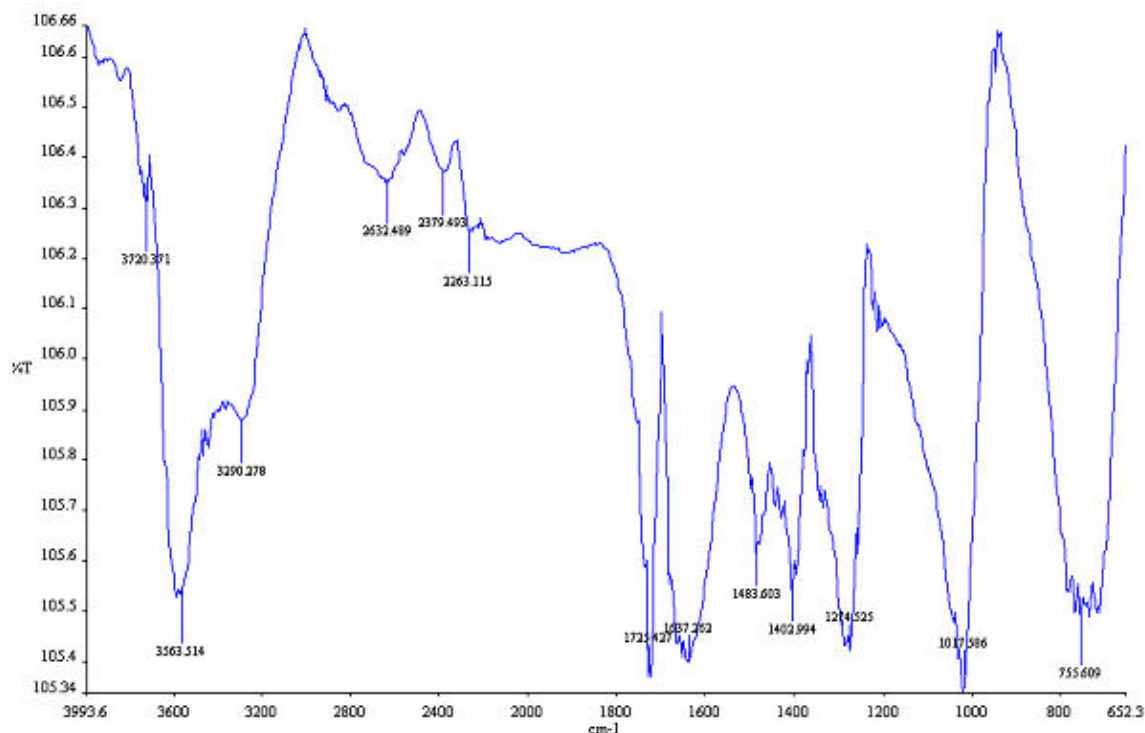


Figure 1: Infra-red spectrum of pyrolysis oil from Eucalyptus wood

#### *Phenols extraction*

Liquid-liquid extraction of phenols was performed on the pyrolysis oil at ambient temperature. This oil was completely soluble in selected standard organic solution and filtration of insoluble materials was not necessary. The extraction was started with an aqueous sodium bicarbonate solution at a pH value of 8.7. The aqueous bicarbonate layer extracted the strong organic acids and highly polar compounds. The extraction was then continued at a pH of about 14 in order to extract the phenolic compounds by an aqueous sodium hydroxide solution at a higher pH. The phenols were regenerated by acidifying the solution with a solution of sulfuric acid 50% by weight to a pH near 6. Additional FTIR analysis of the aqueous layers after standard organic solvent extraction confirmed the present of phenols. The major peaks in the extracted pyrolysis oil from the extraction experiment revealed that the compounds were almost all phenolics.

#### Conclusion

FTIR and GCMS analysis showed that the pyrolysis oil from Eucalyptus wood rich in phenolic compounds that were potential used as a starting material for development of enhanced oil recovery

additive. The overall yield of phenolic compounds was founded at 56.04 area %. Complete recovery of phenols was achieved at a pH of 13 to 14 by using a concentrated alkaline solution.

Table 1: FTIR functional group compositions of pyrolysis oil

Frequency range (cm <sup>-1</sup> )	Bond Type	Family
3650 - 3100	O-H stretching	Polymeric O- H, water impurities
2200 -1950	C≡C stretching	Alkanes
1780 - 1640	C=O stretching	Ketones, aldehydes, carboxylic acids
1680 - 1580	C=C stretching	Alkenes
1550 - 1490	-NO <sub>2</sub> stretching	Nitrogenous compounds
1465 - 1350	C-H bending	Alkanes
1300 - 950	C-O stretching O-H bending	Primary, secondary and tertiary alcohols, Phenols, esters, ethers
900 - 650	O-H bending	Aromatic compounds

Table 2: Identification of chemical compounds in pyrolysis oil by GCMS

Chemical compounds	Area , %	Chemical compounds	Area , %
Phenol	36.18	Triphenylphosphine oxide	12.97
2 methoxy phenol	4.58	4-hydroxy benzoic acid	6.10
2,6-dimethoxy phenol	4.56	4-hydroxy -methyl ester benzoic acid	2.03
2-methoxy -4 methyl phenol	2.39	3-hydroxy -4 methoxy benzoic acid	1.90
4-ethyl -2 methoxy phenol	2.21	2-methyl -ethyl ester propenoic acid	0.43
3-[(trimethylsilyloxy]-phenol	1.96	2-hydroxy-3-methyl-2 cyclopentenone	1.36
2-methoxy -4(1-propenyl ) phenol	1.48	3-ethyl-2-hydroxy-2cyclopentenone	0.25
2,6-dimethoxy-4-(2-propenyl) phenol	1.39	4-hydroxy -3-methoxy benzaldehyde	0.96
2-methyl phenol (o-cresol)	0.51	4-hydroxy-3,5-dimethoxy benzaldehyde	0.42
4-methyl phenol (p-cresol)	0.48	1,4-dimethoxy -2,6-dimethyl benzene	0.41
2-methoxy -4-propyl phenol	0.26	Others	17.07

### References

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