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PYROLYSIS OF BEECH WOOD CATALYSED BY $FeCl_3$: PRODUCTION AND CHARACTERISATION OF BIO-OIL

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Abstract:

The pyrolysis of beech wood in the presence of acid catalyst such as $FeCl_3$ was carried out at the temperatures of 400, 500 and 600°C. The effects of temperature and the catalyst on both product distribution and bio-oil composition were investigated. The compositions of the bio-oils obtained from the catalytic pyrolysis of wood sawdust were identified by GC-MS and ^{1}H-NMR analysis. The bio-oils produced from catalytic pyrolysis of wood contained a wide variety of oxygenated hydrocarbons. Aldehydes were found to be major compounds identified in bio-oils. The results of this study indicated that bio-oil obtained from beech wood sawdust can be used as chemical raw materials.

Key words: *biomass; catalytic pyrolysis; bio-oil; oriental beech.*

INTRODUCTION

Renewable energy is growing importance in satisfying environmental concerns over fossil fuel usage and it's contribution to the Greenhouse Effect. Wood and other forms of biomass, including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available (Bridgwater e*t al.* 2005*,* Bridgwater e*t al.* 2003*)*. Different thermo-chemical conversion processes that include combustion, gasification, liquefaction, hydrogenation and pyrolysis, have been used to convert the biomass into various energy products. The pyrolysis is degradation of biomass by heat in the absence of oxygen which results in the production of charcoal, liquid and gaseous products. Pyrolysis can be used as an independent process for the production of useful fuels and/or chemical (Goyal *et al.* 2008, Desideri *et al.* 2011). Bio-oil as a high-value energy carrier and value-added chemicals obtained through thermo-chemical conversion processes are expected to play an important role in future energy and chemical supply. However, the bio-oil direct applications as fuels are limited by the problems of high oxygen content, high viscosity, corrosion and their thermal instability. Therefore, bio-oils must be upgraded before they can be used in gasoline or diesel engines. Catalytic pyrolysis offers a potential route to modify or upgrade the compositions and qualities of the bio-oil product (Qi *et al.* 2006, Wang *et al.* 2010*,* Nilsen *et al.* 2010). Acid catalysts have been used for improving the quality of the bio-oil by several researchers (Encinar *et al.* 1997, Amarasekara *et al.* 2009, DiBlasi *et al.* 2008). Chen et al. pyrolysis of pine wood sawdust was carried out by microwave heating. Eight inorganic additives (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM–5, H_3PO_4, $Fe_2(SO_4)_3$) were investigated in terms of their catalytic effects on the pyrolysis. It was reported that all the eight additives have increased yields of solid products greatly and decreased yields of gaseous products more or less. Yields of liquid products have not subjected to dramatic change (Chen *et al.* 2008). Özbay et al. produced bio-oil from catalysis pyrolysis. Acids ($AlCl_3$, $TiCl_4$, and $FeCl_3$), bases (NaOH and KOH) and basic salts (Na_2CO_3 and K_2CO_3) were used as catalysts in the pyrolysis process. They determined that bio-oils obtained from the non-catalytic and catalytic experiments contain a large variety of oxygenated hydrocarbons such as phenols, aldehydes, acids, alcohols, ketones and polycyclic aromatic hydrocarbons (PAHs). While the phenol compounds were the major components in the bio-oils. The bio-oil obtained from $FeCl_3$ consisted of aldehydes such as furfural (Ozbay *et al.* 2012). Branca et al. have studied acid catalyzed pyrolysis of biomass for furfural production. The selected acidic catalysts are sulfuric acid (H_2SO_4), zinc chloride ($ZnCl_2$) and ferric sulphate ($Fe_2(SO_4)_3$). They found that the maximum yields of furfural are around 5-6% for the three catalytic treatments (Branca *et al.* 2012).

In the present study, the pyrolysis of Oriental beech (*Fagus orientalis* L.) sawdust was carried out by using acidic catalyst such as $FeCl_3$. The influences of the pyrolysis temperature and the catalyst on the product distributions and chemical composition were examined based on identical conditions.

EXPERIMENTAL

Samples and catalysts

The samples used for this study were the sawdust of Oriental beech (*Fagus orientalis* L.), which grows widely in Turkey. Widespread use of beech wood is to make furniture materials, which produces sawdust. The experimental samples that have a particle size in the range of 0.850–1.60mm. The catalyst used in this study was Lewis acid ($FeCl_3$). The properties of the catalyst were listed in Table 1.

Table 1

The properties of the catalyst

Properties	**$FeCl_3$**
Solubility	920g/L (20°C)
Melting point	306°C
Molar mass	162.20g/mol
Density	2.9g/cm^3 (20°C)
Bulk density	1000kg/m^3
pH value	1 (200g/L, H_2O, 20°C)

Pyrolysis experiments

Pyrolysis experiment was carried out in a fixed-bed reactor under nitrogen atmosphere. As shown in Fig.1, it consisted of a stainless steel reactor (diameter 60mm and height 210mm) seated in an electrically heated furnace and was connected to two water-cooled condensers with liquid traps. In each test, samples of 50g (dry basis) and the required amount of catalysts in concentration 10% of the samples were placed into the reactor. The system was heated from room temperature to a final temperature of 400, 500 or 600°C and kept at the temperature for 60min in order to allow sufficient time to finish pyrolysis. The volatile products

were swept by nitrogen gas from reactor to collection flasks. The pyrolysis products were classified into three groups: gas, bio-oil and bio-char. The liquid phase consisted of aqueous and oil phases which were separated and weighed. After pyrolysis, the solid char was removed and weighed, and then the gas yield was calculated by difference.

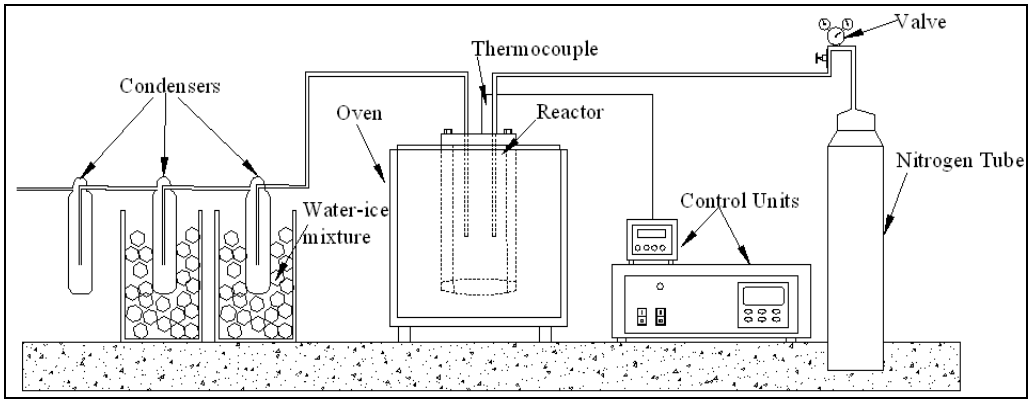

Fig. 1
A schematic diagram of the pyrolysis setup.

Bio-oil characterization

Bio-oil was extracted with an equal quantity of diethyl ether. The diethyl ether extracts were analyzed by GC-MS and ^{1}H-NMR. The separation was made on a 30m×0.25mm i.d. phenyl methyl siloxane capillary column HP-5MS using a 6890 Gas Chromatograph Agilent. The GC oven temperature was programmed to start at 40°C, held for 10min, then raised at a rate of 2°C/min to 170°C, held for 5min, then raised to 250°C at a rate of 8°C/min held for 15min, then raised to 300°C at a rate of 15°C/min, and held at this final temperature for 10min. The injector temperature was 250°C with split mode. A 1ml/ min of helium was used as the carrier gas. The end of the column was directly introduced into the ion source of Agilent 5973 series mass selective detector operated with electron impact ionization mode. The data acquisition system used was G1035A software with a NIST library. ^{1}H-NMR spectrum was obtained at a H frequency of 300MHz using the Bruker Ultrashield apparatus.

RESULT AND DISCUSSION

Product yields

Fig. 2 shows the product distribution, which was obtained from the pyrolysis of beech wood sawdust at temperatures of 400, 500 and 600°C. In pyrolysis experiments, both temperature and catalyst affected the product distribution.

In the pyrolysis process, the temperature is known to be an important parameter in the conversion of biomass into bio-oil, char and gas (Williams *et al*. 1996). According to Fig. 2, the bio-oil yields were higher at the temperatures of 600°C than those of 400 and 500°C. The maximum bio-oil yields obtained from the pyrolysis of beech wood sawdust with $FeCl_3$ was 47.5% at 600°C. The gas yield continuously increased from 22.3 wt.% to 23.2 wt.% as the temperature increased from 400°C to 600°C. The use of $FeCl_3$ led to an increase in the yields of gas and bio-char against a decrease in the bio-oil yield. The higher pyrolysis temperatures have been associated with secondary cracking reactions of the pyrolysis gases to produce increased gas yields and reduced bio-oil yield (Williams *et al*. 2000). Previous studies with similar biomass samples showed that temperatures between 500 and 600°C gave the highest bio-oil yields (Peng *et al*. 2012, Demiral *et al*. 2011, Pütün *et al*. 2007).

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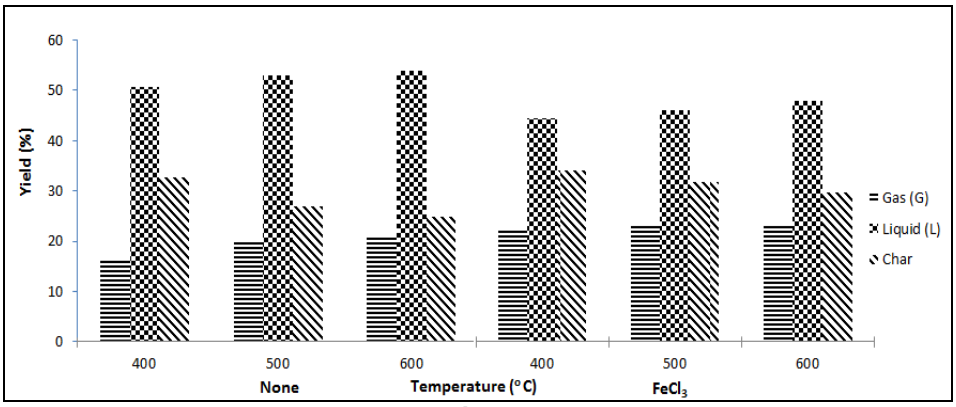

Fig. 2

Product yields from pyrolysis of beech wood sawdust

(The results of non-catalytic pyrolysis were taken from the study that made by Özbay and Özçifçi (2012) with the aim of comparing differences between catalytic and non-catalytic pyrolysis).

Chemical Characterization of Bio-oil

The bio-oils, obtained from catalysed pyrolysis of beech wood sawdust were analyzed by GC–MS. Table 2 listed the categories of major bio-oil compounds were grouped as aldehydes, acids and esters, alcohols, benzene derivates, ketones, phenols, alkanes and polycyclic aromatic hydrocarbons (PAHs).

Table 2

Classification of identified compounds in the bio-oils from the non-catalytic and catalytic pyrolysis of beech wood

Compounds	None	$FeCl_3$
Aldehydes	**7,01**	**63,64**
Acids and Esters	**5,29**	**2,79**
Alcohols	**7,92**	**0,50**
Ketones	**7,75**	**4,03**
Benzene Derivatives	**0,71**	**0,27**
PAH	**-**	**0,39**
Phenol	**31,00**	**9,20**
Alkanes	**0,30**	**0,02**
TOTAL	**59.98**	**80.84**

(The results of non-catalytic pyrolysis were taken from the study that made by Özbay and Özçifçi (2012) with the aim of comparing the differences between catalytic and non-catalytic pyrolysis).

According to Fig. 3 the bio-oil obtained from non-catalytic pyrolysis of beech contains mainly phenolic compounds, such as 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 2-methoxy-4-ethyl-phenol, 2,6-dimethoxy-phenol, 3,4-dimethoxy-phenol, 2-methoxy-4-(1-propenyl)-phenol (Özbay and Özçifçi 2012). Some other studies concerning pyrolysis of biomass also show quite similar distribution of organic components to ours (Junming *et al.* 2008, Wang *et al.* 2009, Lu *et al.* 2010). Two dominant organic components identified in the bio-oil from pyrolysis of $FeCl_3$ treated beech sawdust are both furfural and 5-Methyl-2-furancarboxaldehyde. The yield of furfural was increased by the $FeCl_3$ catalyst. The Furfural is a typical pyrolytic product from both of cellulose and hemicellulose. It is an useful organic reagent for the production of medicines, resins, food additives, fuel additives and other special chemicals. Previous studies have revealed that the formation of furfural can be increased in various acid-catalyzed pyrolysis processes (Lu *et al.* 2011).

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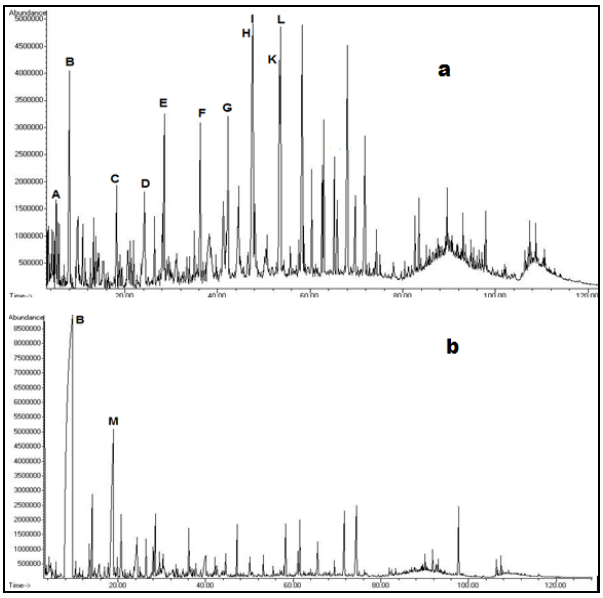

Fig. 3

Representative total ion chromatographs of bio-oils obtained from the pyrolysis of beech wood sawdust (a: non-catalytic, b: $FeCl_3$) [A: Toluene, B: Furfural, C: 3- Methyl-2-Cyclopenten-1-one, D: 2-Hydroxy-3- Methyl-2-cyclopenten-1-one, E: 2-Methoxy-phenol, F: 2-Methoxy-4-methyl-phenol, G: 2-Methoxy-4-ethyl-phenol, H: 2,6- Dimethoxy-phenol, I: 3,4- Dimethoxy-phenol, K: 2-Methoxy-4-(1-propenyl)-phenol, L: 4 Hydroxy-3-methoxy-benzoic acid, M: 5-Methyl-2-furancarboxaldehyde]. (The results of non-catalytic pyrolysis were taken from the study that made by Özbay and Özçifçi (2012) with with the aim of comparing the differences between catalytic and non-catalytic pyrolysis).

Fig. 4 represents the ^{1}H-NMR spectra of bio-oils obtained from beech wood sawdust by non-catalytic and catalytic pyrolysis. Aldehydes peaks were noticed peaks in the resonances between range of 9-10ppm. Resonances between 6.5–9ppm were assigned to aromatic structures. Resonances between 5–6.5ppm were indicates that the aromatic species were largely phenolic compounts. Methylene protons were observed in the bio-oil and their typical peaks were in the resonances between range of 3.3–4.5ppm. These ^{1}H-NMR spectra results were in agreement with GC-MS analyses results.

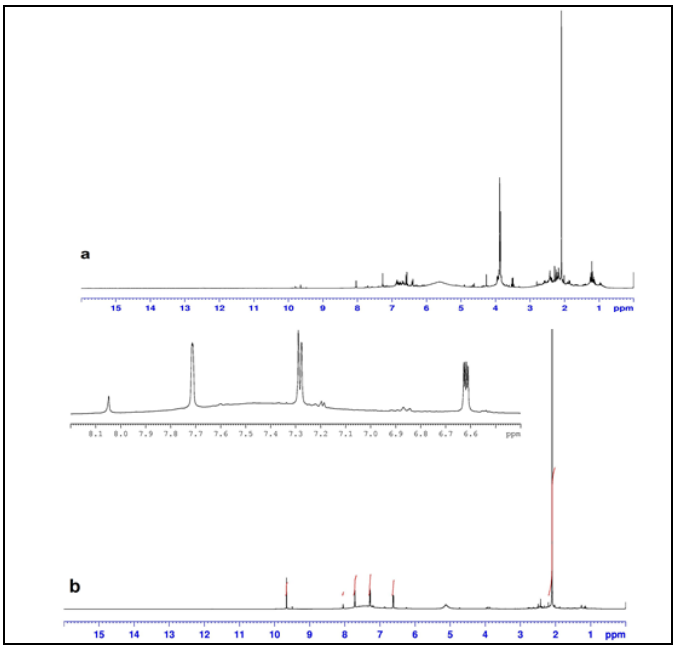

Fig. 4

^{1}H-NMR spectra of the bio-oils (a) None, (b) $FeCl_3$

(The results of non-catalytic pyrolysis were taken from the study that made by Özbay and Özçifçi (2012) with the aim of comparing the differences between catalytic and non-catalytic pyrolysis).

CONCLUSIONS

Pyrolysis of beech wood sawdust was carried out at 400, 500, and 600°C in the presence of $FeCl_3$ catalyst. The product distributions from the pyrolysis of beech wood sawdust were changed depending on both the catalyst and temperature.

Catalyst significantly changed the compositions of bio-oil. With the use of $FeCl_3$, the yields of aldehydes were increased, and the yield of alcohols and phenols were notably decreased. In particular, the content of aldehydes were observed to be the main component and its content higher than non-catalytic process. Bio-oil obtained from beech wood sawdust can be used as synthetic liquid fuels or chemical raw materials.

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