

BIO-FUELS AND MAGNETIC ACTIVATED CARBON PRODUCTION VIA CO-PYROLYSIS OF LIGNIN AND FERROUS SALTS AND STEAM ACTIVATION OF PRODUCED BIO-CHAR

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ABSTRACT

The objective of the present work is co-production of bio-fuels and magnetic activated carbon (MAC) materials via fast pyrolysis of lignin and ferrous salts mixtures and steam activation of pyrolysis char. Specifically, the effect of the addition of the ferrous salts on the quality of biofuels including bio-gas and bio-oil is investigated. The effect of the addition of the ferrous salts on the mass loss rate of bio-chars during the steam activation process is also investigated. Results show that for the fast pyrolysis process, the addition of ferrous salts leads to a hydrogen rich bio-gas and non-guaiacols containing bio-oil production. The cracking effect of irons for the fast pyrolysis vapors is believed to be the dominated reason. For the steam activation process, the addition of the ferrous salts causes a relatively low mass loss rate of bio-chars, because steam can oxidize iron to form magnetite.

Keywords

Bio-fuel, Magnetic activated carbon, Iron, Cracking

1 INTRODUCTION

Lignin is the second highest component in biomass and one of few aromatic sources in nature. Annual production of waste lignin from paper/pulp industries is estimated to be around 70 million tons globally. However, around 95% of these technical lignin is directly burned as low-value fuel for energy compensation. This is a great waste of energy materials. Therefore, it is quite urgent to develop high efficient techniques to convert lignin to add-value products [1].

Pyrolysis of lignin is regarded as one promising thermochemical routine for lignin conversion [2]. After a fast pyrolysis of lignin process, bio-gas, bio-oil and bio-char are produced. Wherein, bio-gas and bio-oil can be

used as alternatives of fossil fuels directly or after upgradation. Bio-char is carbon-rich materials which can be burned directly or can be used as carbon resources for functional carbon materials production.

Bio-chars and bio-char-derived activated carbons have great utilization potentials in a wide applications such as adsorption, catalysis and energy storage due to their porous structure [3]. Nowadays, addition of magnetic metal components to bio-char or char-derived activated carbons is getting more and more attentions, because the produced magnetic activated carbon (MAC) materials are easy to isolate from a system. Moreover, the adsorption capacity for anionic pollutes of MAC materials can be greatly enhanced with the assistance of surface magnetic metal oxides [4].

Most of papers only focus on the yield and the quality of final products i.e., MAC materials. However, yield and quality of bio-oil and bio-gas, which are produced during the initial pyrolysis/carbonization of raw biomass materials process are usually overlooked. Moreover, if the raw biomass materials are premixed or pre-impregnated with magnetic metal precursors the metal ions ought to have catalytic effects on the pyrolysis vapors, which will definitely influence yield and quality of the produced bio-oil and bio-gas [5].

In the present work, a novel process for co-production of bio-fuels and MAC materials from lignin and ferrous salts mixtures are investigated. Instead of a slow heating (10°C/min) carbonization process, a fast pyrolysis process with higher heating rate was performed for lignin carbonization. The main aim is to increase the yield and quality of bio-fuels i.e. bio-gas and bio-fuel. Steam activation of bio-chars was then performed to produce the MAC materials. Investigation of the catalytic effect of ferrous salts on the pyrolytic products production and

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the effect of ferrous salts amount used and the way to add them into lignin on the properties of the final materials is the main focus of the present work.

2 MATERIAL AND METHODS

2.1 Material

The carbon source in this work is lignin, which has been isolated from a pulping process. Specifically, lignin is the Kraft lignin that is isolated from spruce according to the LignoBoost process. Before the trials, the lignin was dried at room temperature to reach a stable moisture content around 2%. Thereafter, it was sieved and the finest particles smaller than 0.125mm were used. Ferrous salt, i.e. FeSO₄, which was bought from Sigma-Aldrich, was used as a magnetic component precursor. It was ground and sieved before being used. Samples with a similar size range (< 0.125mm) as lignin were used in the experiments.

2.2 Methods

Before testing, 20g lignin was mechanically mixed with 3.8g and 7.6g ferrous salts. Iron contents in these two cases are around 4 wt. % and 8 wt. %. As a comparison, 20g lignin was also added into an equal-volume-solution, which contains 7.6g ferrous salts. After being stirred well, formed lignin and ferrous salts slurry was kept for impregnation overnight at room temperature. After that, the slurry was put into oven in which the temperature was set as 60°C to dry for a duration time of 12 hours.

Fast pyrolysis of lignin and ferrous salts mixtures was performed in a modified fixed bed reactor. Nitrogen was used as the carrier gas and was flushed from the top of the reactor at a flow rate of 0.5 l/min. A thermocouple, which could be moved along the furnace, was connected to the sample holder. In this way, the heating curve of the lignin sample could be recorded via a lab view workstation during testing. Before the experiment, the sample was kept in the cooling zone on top of the reactor. In this case, although the furnace was preheated to a high temperature, the sample temperature could always be maintained at approximately 15°C. When the temperature of the furnace reached the reaction temperature of 800°C, the sample basket was exposed to the high-temperature zone and kept in the high-temperature zone for 60 minutes after the temperature of the sample had reached 800°C. Afterwards, the sample was returned to the cooling zone. The produced pyrolysis vapors were flushed from the bottom of the tube and through a series of glass bottles, a circulating condenser tube and a flash cone. The glass bottles were placed in a water and isopropanol mixture, which were held at a low temperature by a cooling-liquid circulation

pump. A circulating condenser tube was directly connected to the pump of the cooling-liquid circulation bath pump for circulation of the cooling liquid. The flash cone was covered with ice bags for cooling. The temperature of the water and isopropanol mixture in the cooling-liquid circulation pump bath was approximately -15°C. The temperature of the flash cone covered by the ice bags was approximately -2°C. Subsequently, the condensable vapors were collected in the glass bottles, condenser tube and flash cone. The remaining noncondensable gases were passed through a gas meter to measure their volume. Then, they were collected in a gas bag for later analysis by Micro Gas Chromatography. The sample holder, glass bottles, condenser tube and flash cone were weighed before and after the experiment to obtain the char and total liquid yields.

Steam activation of bio-char obtained from the fast pyrolysis process was performed at 800°C in the present work. The CMs were firstly put in the specially designed container which, in turn, was placed in the muffle furnace. Nitrogen with a flow rate of 50 ml/min was supplied during the heating process, but it was switched to steam after the furnace reached a temperature of 800°C and the temperature got stable. Steam-bio-char ratio of 4 was used for all cases.

3 RESULTS AND DISCUSSIONS

3.1 Results

3.1.1 Fast pyrolysis of lignin and ferrous salts mixtures

3.1.1.1 Mass balance

Table 1. Bio-gas, bio-oil and bio-char yields obtained after fast pyrolysis of different lignin and ferrous salts mixtures.

Lignin+FeSO ₄ (Wt. + Wt.)	Bio-gas (Wt. %)	Bio-oil (Wt. %)		Bio-char (Wt. %)
		Aqueous phase	Organics phase	
20+3.8	30.73	20.47	8.66	36.48
20+7.6	30.18	18.18	7.70	37.09
20+7.6 IMG	26.79	20.08	4.88	47.79

Bio-gas, bio-oil and bio-char yields obtained after fast pyrolysis of different lignin and ferrous salts mixtures are shown in table 1. It can be seen that mechanically mixing 20g lignin with 3.8g and 7.6g ferrous salts induce similar yields distribution of bio-gas, bio-oil and bio-char. This indicates that the amount of ferrous salts has little effect on the pyrolytic products yield distribution. However, when 20g lignin is impregnated in 7.6g ferrous salts solutions, bio-gas, bio-oil and bio-char yields distribution obtained after a fast pyrolysis process are quite different with that obtained when 20g lignin is mechanically mixed with ferrous salts. Notably, bio-char yield obtained after fast pyrolysis of mixture formed via impregnating 20g lignin into 7.6g ferrous salts solutions is as high as

47.79%, which is more than 10% higher than that obtained after fast pyrolysis of mixtures formed via mechanically mixing 20g lignin and ferrous salts. Therefore, it seems that impregnating lignin into ferrous salts solutions helps to fix carbon during the fast pyrolysis process.

3.1.1.2 Gas composition

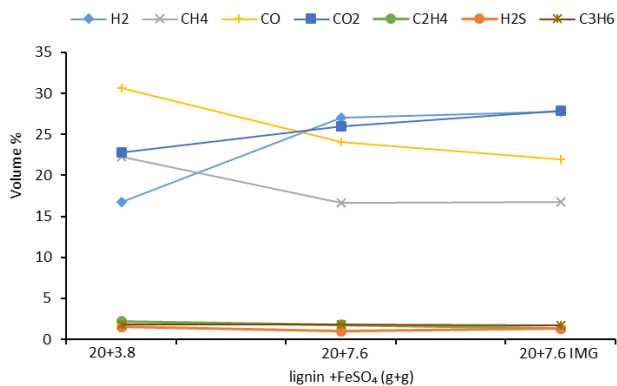


Figure 1. Volumetric percentage distribution of pyrolytic gases obtained after fast pyrolysis of lignin and ferrous salts mixtures.

Composition of non-condensable pyrolytic gases has been analyzed by Micro Gas Chromatography instrument. The results are shown in figure 1. It can be seen that H₂, CH₄, CO and CO₂ are the main gas components in the pyrolytic gases obtained after fast pyrolysis of all lignin and ferrous salts mixtures. All these four gas components occupy a volumetric percentage higher than 15% in all cases. However, volumetric percentage of specific gas components among different cases is different. As shown in figure 1, mechanically mixing 20g lignin and 7.6g ferrous salts and impregnating 20g lignin into 7.6g ferrous salts solutions induce similar volumetric percentages of H₂, CH₄, CO and CO₂, which are around 28%, 17%, 23% and 27%, respectively. However, compared to these two cases, mechanically mixing 20g lignin and 3.8g ferrous salts induces around 11% H₂ lower, 5% CH₄ higher, 7% CO higher and 5% CO₂ lower in volumetric percentages. In addition to the above four gases, relatively low amount of C₂H₄, C₃H₆ and H₂S are also detected in the pyrolytic gases obtained after fast pyrolysis of all lignin and ferrous salts mixtures. Moreover, the volumetric percentages of these three gas components are similar and lower than 5% among all cases.

According to the literature, only trace amount or even no H₂ can be detected in the pyrolytic gases obtained after fast pyrolysis of pure lignin [6]. However, fast pyrolysis of lignin and ferrous salts mixtures induce at least 17% volumetric percentage of H₂ in the present

work. Moreover, volumetric percentage of H₂ obtained after fast pyrolysis of lignin and ferrous mixtures containing 7.6g ferrous salts are around 11% higher than that obtained after fast pyrolysis of lignin and ferrous salts mixture containing 3.8g ferrous salts. All these indicate that the addition of ferrous salts causes a H₂ rich gas production. The increase of H₂ volumetric percentage is believed mainly owing to the catalytic effect of iron which has been well documented as good cracking catalyst in the literature [5].

3.1.1.3 Organic oil composition

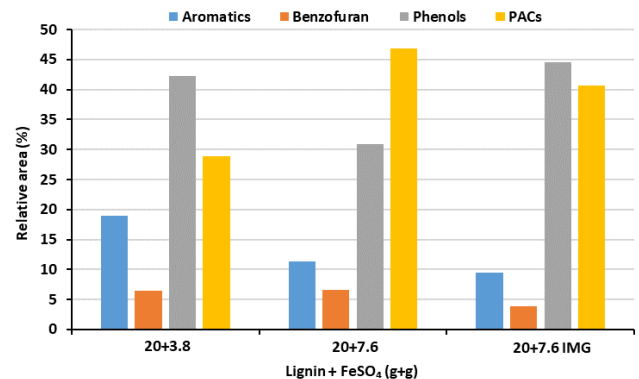


Figure 2. Relative area of compounds in organic oil obtained after fast pyrolysis of lignin and ferrous salts mixtures.

Organic oil composition has been analyzed. The compounds detected are divided into four major categories: aromatics, benzofuran, phenols and polycyclic aromatic compounds (PACs). Summary relative area of compounds belonging to different categories are shown in figure 2.

According to figure 2, no guaiacol-type compounds can be detected after fast pyrolysis of all lignin and ferrous salts mixtures. As mentioned before, lignin used in the present work was isolated from one type of softwood i.e. spruce. According to the literature, lignin from softwood mainly leads to a guaiacol rich bio-oil production after a fast pyrolysis process [7]. These suggest that addition of ferrous salts greatly promote the conversion of guaiacol-type compounds. Such promotion seems also to be owing to the catalytic effect of irons. The strong cracking effect promote the conversion of guaiacols. As a result, the production of aromatic, phenol and PACs are significantly promoted.

3.2 Steam activation of bio-char

Table 2 Mass loss of the steam activation process.

Lignin+FeSO ₄ (Wt. + Wt.)	Mass loss (Wt. %)
20+3.8	26.25
20+7.6	27.50
20+7.6 IMG	35.00

As mentioned before, a steam activation process was performed to activate the bio-chars obtained from fast pyrolysis of lignin and ferrous mixtures. The aim is to produce the MAC materials which are easy to be isolated from a system. As is known that the mass loss of the activation process is crucial since it determines the porosity of the final activated carbon materials. Mass loss results of different steam activation processes performed in the present work are shown in table 2.

It can be seen that steam activation of bio-char obtained after fast pyrolysis of mixture formed via mechanically mixing 20g lignin and 3.8g ferrous salts induces a mass loss around 26.25% and steam activation of bio-char obtained after fast pyrolysis of mixture formed via mechanically mixing 20g lignin and 7.6g ferrous salts induces a mass loss around 27.50%. Steam activation of bio-char obtained after fast pyrolysis of mixture formed via impregnating 20g lignin into 7.6g ferrous salts solutions induces the highest mass loss which is around 35.00%. Compared with the mass loss results of steam activation process using similar steam-to-char-ratio in the literature, mass loss of all these three cases are quite lower. Addition of ferrous salts is also believed to be the main reason. During the fast pyrolysis process, ferrous salts are inevitably decomposed to form Fe₂O₃ at a temperature higher than 500°C. Moreover, during the carbonization process at 800°C formed Fe₂O₃ can be reduced by carbon to form iron. During the steam activation, steam reacts with carbon to form pore. At the same time, irons are exposed on the surface of pores and immediately oxidized by steam to form magnetite. This indicates the existence of iron will cause a mass increase but not mass loss. This is also the reason why the produced MAC materials have quite strong magnetic properties.

4 CONCLUSIONS

In this work, fast pyrolysis of mixtures formed via mechanically mixing lignin and ferrous salts and mixtures formed via impregnating lignin into ferrous salts solutions were first performed to produce bio-fuels. Steam activation of produced bio-chars were then performed to produce MAC materials.

Results show that amount of ferrous salts has little effect on the pyrolytic products yield distribution but impregnating lignin into ferrous salts solutions seems to

be effective to fix carbon during the fast pyrolysis process. The addition of ferrous salts leads to a hydrogen rich bio-gas and non-guaiacols containing bio-oil production. The cracking effect of irons for the fast pyrolysis vapors is believed to be the dominated reason. The addition of the ferrous salts also causes a relatively low mass loss rate of bio-chars during the steam activation process, because steam can oxidize iron to form magnetite.

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