Technical and Economical Feasibility of Pyrolysis of Kraft Lignin

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ABSTRACT

This research project discusses the technical and economical feasibility of converting kraft lignin to value-added chemicals. Two pyrolysis techniques were implemented: conventional pyrolysis using classical heating and microwave pyrolysis using electromagnetic irradiation. The product distribution and the composition of the bio-oil from the conventional pyrolysis were compared against those from the microwave pyrolysis. Gas chromatography−mass spectrometry analysis was carried out to identify the organic compounds in the obtained oil. To estimate the minimal selling price of the lignin pyrolysis oil and the expected cumulative cash flow at the end of the life cycle of the plant, a first step economics evaluation was completed using the method “net present worth.” Subsequently, different scenarios for reducing the estimated price, which would help for taking a place among the fossil fuel-based chemicals, were debated.

Keywords: pyrolysis, kraft lignin, bio-oil, economics

1 INTRODUCTION

In North America, the forest industry is one of the cornerstones of the national economy. In Canada, for example, it contributes $80 billion per year to Canada’s total gross domestic product and provides more than 900,000 jobs across the country. Presently, however, this industrial sector is at a crossroads as it is facing unexpected challenges due to competition from low-cost sources of wood and a decline in demand. One of the most promising paths to ensure a sustainable future for the industry is the production of value-added products in addition to the traditional commodity. This approach leads to diversifying the range of products from the forest industry and, consequently, opens the door to new markets.

In the papermaking process, the wood chips and an aqueous solution are cooked in a digester to separate lignin from the feedstock. Thereafter, lignin is produced as weak black liquor (at 15-20 wt% of solid concentration) whereas the remaining material, which consists of wood fibres, becomes paper. The most popular technique that deals with black liquor is to increase the solid concentration and then burn it in a recovery boiler. This technique mainly produces heat energy and recycles the inorganic chemicals for reuse in the pulping process. Another technique, which is precipitating lignin from black liquor, has been established to enable expanding pulp and paper production without having to expand the capacity of the recovery boiler. Accordingly, the production of lignin is dramatically growing, which demands more attention for discovering new techniques for dealing with the massive quantity of lignin produced worldwide.

Lignin is the only renewable source of aromatics in nature and the third most abundant natural polymer after cellulose and hemicellulose [1]. The structure of lignin, which is a complex heterogeneous aromatic polymer with many functional groups, makes lignin a promising material for the production of a variety of commercial products. Chemical, biological, and physical technologies are the main methods for the production of lignin-based products. Pyrolysis, which is the thermal decomposition of chemical bonds of a target material by supplying heat energy in an oxygen-free environment, is one of the techniques applied in the chemical technology. Generally speaking, pyrolysis of lignin produces three main products: condensable gas, solid, and non-condensable gas. The condensable gas product (bio-oil) is mostly aromatics containing useful and valuable phenolic compounds, such as phenol, dimethylphenol, guaiacol, catechol, and syringol [2]. These phenols can be used in many industrial applications, for example, the production of phenol formaldehyde resins, the synthesis of pharmaceuticals, gasoline additives, antioxidants, food additives, polymerization initiators, pesticides, and colorants [2]. The solid product (bio-char) is mostly carbon and can be used in a wide range of applications: tire manufacturing processes, soil additive, activated carbon, and solid fuel. The non-condensable gas (bio-gas) is combustible, which can be burned to generate the heat energy that is required for performing the pyrolysis process. In addition, it could be used in the Fischer Tropsch process for the production of several hydrocarbon products.

Although there are few studies on the production of highly priced lignin-based products, such as conductive materials, pyrolysis is still the only technique that can deal with the huge quantity of lignin produced in pulp mills across the globe. Therefore, it is of great interest to efficiently implement pyrolysis to convert lignin into value-added chemicals that could replace petrochemicals in many applications. Such an approach does not only lead to dealing with the huge quantity of lignin produced across the world but also decreases the consumption of fossil fuel based chemicals and, therefore, addresses the problems due to the rapid increase in the price of petrochemicals.

In this research project, pyrolysis of kraft lignin was accomplished by applying two different techniques: conventional pyrolysis (CP) using traditional heating and microwave pyrolysis (MWP) using electromagnetic irradiation. Gas chromatography−mass spectrometry (GC-MS) was performed on the bio-oil to understand the composition of the obtained chemicals. Subsequently, a first step economics evaluation was completed for estimating the minimal selling price of the lignin pyrolysis bio and the expected cumulative cash flow at the end of the life cycle of the plant.

Such studies would present valuable insight for the industrial sectors to encourage them to pursue the idea or guide them in another direction to deal with lignin.

2 EXPERIMENTAL WORK

2.1 Raw Material

In this work, the raw material was softwood kraft lignin supplied by FPInnovations, Quebec, Canada. It was characterized by CHNS analysis: C=63.27%, H=5.79%, N=0.07%, and S=1.56%, and proximate analysis: fixed carbon=37%, volatiles=62%, and ash=1%. To get a better understanding for the obtained products as well as the raw material, the ^{13}C and ^{31}P NMR analyses were performed on the virgin material and reported in Farag et al. 2013, kindly refer to that reference for the full details.

Since bio-char is a strong microwave-to-heat convertor, it was mixed with the virgin material for enhancing the heating processes [3-5]. The concentration of the bio-char in the initial payload mass was chosen in a way that gives a heating rate similar to that of CP.

2.2 Experimental Setup

In the case of MWP, the experimental work was carried out using a bench scale microwave-oven, while in the case of CP a conventional heating oven was used. A quartz semi-batch reactor was used after connecting its outlet with a condensation system kept at -18 ^{o}C using a traditional freezer. In order to prevent a vapor condensation barrier to the condensation system, the line that connects the reactor with the condensers was kept at 200 ^{o}C using external-temperature heat cables. The detailed information regarding the experimental setup can be found in the references [6-8].

3 RESULTS AND DISCUSSION

3.1 Product Distribution

Figure 1 demonstrates the product distribution for the CP and MWP of kraft lignin. The presented values are the average of three repetitions performed under the same conditions, and the error bars are the standard deviations. The yield of each run was calculated based on the initial dry mass basis of the feedstock.

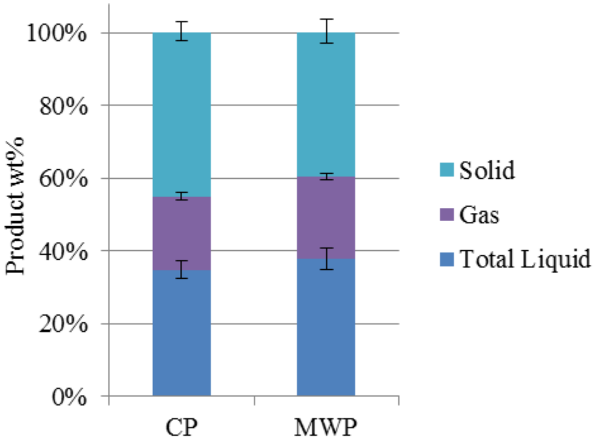

Figure 1: Product distribution of the conventional and microwave pyrolysis of kraft lignin

As one see, applying electromagnetic irradiation in pyrolysis produced a liquid yield that is slightly higher than what was obtained from the conventional pyrolysis, 38 wt% and 35 wt%, respectively. If the uncertainty of the experimental data is taken into account, the effect of microwaves on the bio-oil yield becomes insignificant. On the other hand, the solid residue obtained from MWP is 15 wt% (relative to the char yield of the CP) less than what was obtained from CP. This difference might be the consequence of the heat and/or mass transfer limitations taking place in the conventional heating processes and considered one of the main issues in such a process. Since the bio-gas yield was calculated by subtracting the liquid and solid yields from the initial lignin mass, its yield is related to the yield of the solid and liquid products. Thus, its interpretation is implicitly included in the previous explanation.

In fact, a quantitative comparison between the product distributions from the applied pyrolysis techniques is somehow misleading since it does not consider the quality aspect. Therefore, further information regarding the composition of the produced bio-oils is discussed.

3.2 Bio-oil Composition

As a first step toward a qualitative analysis, the water content in all the liquid samples (12 samples in total: 6 oil phases and 6 aqueous phases) was determined. The obtained data was processed for calculating the yield of the organics and water products in each of the liquid samples, as manifested in Figure 2. The error bars shown in the figure are the standard deviation.

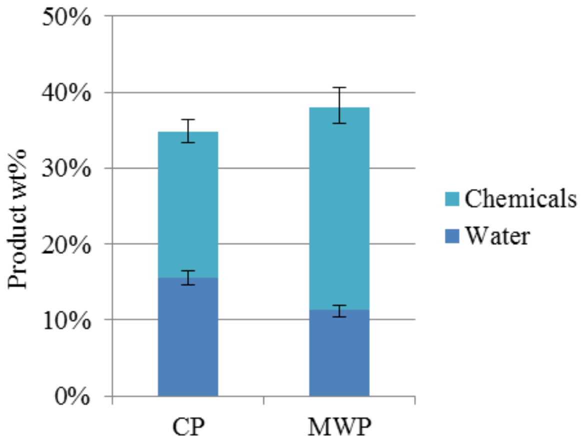

Figure 2: Yields of the chemicals and water products in the produced oils

It is evident that the impact of microwave irradiation on the composition of the produced oil is considerable although its influence on the liquid yield is not confirmed. The organics yield obtained from microwave-assisted pyrolysis is 42 wt% (relative to the organics yield from the CP) more than what was achieved from the classical pyrolysis. Consequently, the yield of the produced water was 31 wt% (relative to the water yield of the CP) less than that of the traditional pyrolysis.

Since conventional heating is a superficial heating process, which in most cases presents a surface hotter than the core, it would lead to further degradations for the pyrolysis vapor. This cleavage of the chemical bonds might be responsible for the decomposition of the aliphatic hydroxyl groups and, as a result, increase the formation of water during pyrolysis, kindly refer to Figure 3. Farag et al. 2014 believe that the decomposition of the OH bonds is mostly attributed to forming water and/or unsaturated sites and, accordingly, it results in a decrease of up to 90% in the concentration of the OH aliphatic side chains [7]. On the other hand, microwave heating is a volumetric energy transfer mechanism, which under controlled conditions presents a surface hotter than the core [9]. This aspect would lead to preserving the structure of the obtained products and, therefore, would produce less water yield compared to the classical pyrolysis.

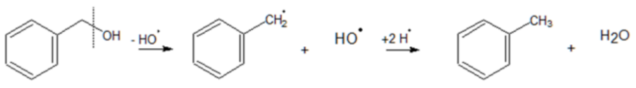

Figure 3: A suggested degradation pathway for the aliphatic hydroxyl group

To obtain further information regarding the composition of the produced bio-oils, GC-MS analysis was performed on the liquid samples. The obtained data was processed to calculate the yield of the common chemical groups, as shown in Figure 4.

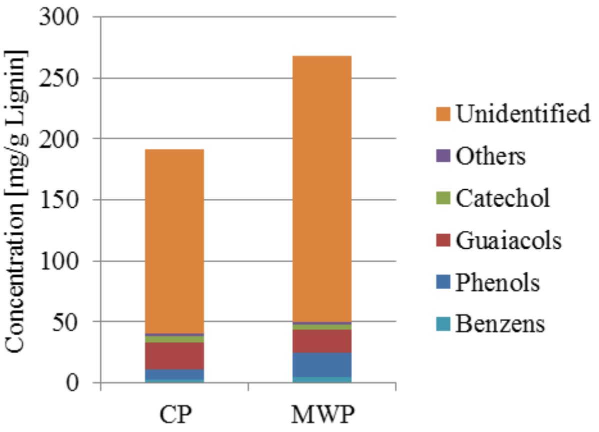

Figure 4: Identifies chemical families using a gas chromatography−mass spectrometry

It is not an exaggeration to claim that MWP produces the maximum yield of both the identified and unidentified chemical compounds. The obtained phenols' yield is more than twice that measured in the CP oil. This means that employing MWP in pyrolysis would lead to improving the quality of the obtained product. However, further investigations to confirm this statement are needed.

3.3 Estimating the Selling Price of the Lignin Pyrolysis Oil

To estimate the selling price of the obtained bio-oil, a first step economics evaluation for converting lignin to value-added chemicals was carried out. An on-site CP plant was designed, and the updated total capital investment was calculated. The main sections of the designed plant are pre-treatment, pyrolysis, condensable gas recovery, and combustion. To calculate the mass and energy of each section, Aspen PLUS^{TM} applications were used. The method "Net Present Worth," which equals the result of subtracting the present capital investments from the present worth of the cash flows, was applied [10].

The above mentioned preliminary economic assessment leads to appraising the profitability of an investment, which is the basis for selecting or rejecting the investment. It should be noted that an accuracy of 20-30% is expected in such assessments [10-12].

The hypotheses of this economics model include 25% of the applied tax, 9% of the discount rate, 30% of the minimum acceptable rate of return, 10 years of the investment period, and 7000 hours/year of the low average operating conditions. $14M was estimated for the total capital investment, considering 100 t/d for the capacity and a working capital of 15% of the total capital investment. $500/t was considered for the purchase price of the raw material. The kinetic parameters of pyrolysis were obtained from the study published by Farag et al. 2014 [13].

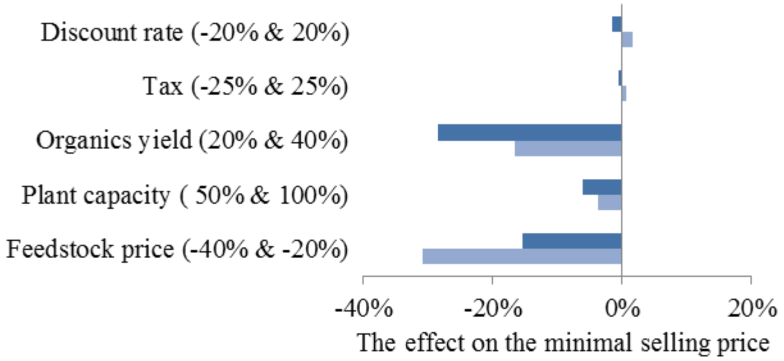

Figure 5: Effect of the crucial variables on the selling price of the kraft lignin pyrolysis oil

Based on the above hypotheses, the bio-oil from the pyrolysis of kraft lignin can be sold at 3200 $/t. The cumulative cash position during the 10-year plant life span shows that the expected cumulative cash flow at the end of the life cycle of the plant is $9M. As a matter of fact, this price could lead to challenging the replacement of the lignin pyrolysis oil by the fossil fuel-based chemical because the estimated selling price is about twice that of the fossil fuel-based products, such as phenols. The sensitivity analyses shown in Figure 5 explains that using a raw material at a low purchase cost in addition to enhancing the organics yield in the bio-oil will dramatically decrease the minimum selling price of lignin pyrolysis oil. In addition, the capacity of the designed plant, estimated tax, and discount rate do not affect the selling price as much as the above-mentioned variables. Therefore, further investigations for presenting lignin at a low purchase cost and to enhance the yield and composition of the lignin pyrolysis oil are essential. In addition, new applications for the produced bio-char will help for overcoming this issue.

4 CONCLUSION

The technical and economical feasibility of the pyrolysis of kraft lignin to value-added chemicals has been discussed. The key conclusion includes that the impact of the electromagnetic irradiation on the yield of the lignin pyrolysis oil could not be confirmed. Microwave pyrolysis looks like it preserves the structure of the pyrolysis vapor and, therefore, its effect on the quality aspect is considerable. According to a first step economics evaluation, the obtained bio-oil from pyrolysis of lignin might not take a competitive place among the fossil fuel based chemicals due to the uncompetitive minimum selling price and the cash flow calculated at the end of the plant life span.

REFERENCES

[1] Farag, S., DÉPARTEMENT DE GÉNIE CHIMIQUE, Philosophiae Doctor, 2013.
[2] Fu, D., et al., Bioresource Technology, 154(0), 101-108, 2014.
[3] Undri, A., et al., Fuel, 116(0), 662-671, 2014.
[4] Undri, A., et al., Journal of Analytical and Applied Pyrolysis, 105(0), 35-42, 2014.
[5] Domínguez, A., et al., Bioresource Technology, 97(10), 1185-1193, 2006.
[6] Farag, S. and J. Chaouki, Applied Thermal Engineering, (0), 2014.
[7] Farag, S., et al., Journal of Analytical and Applied Pyrolysis, 109(0), 249-257, 2014.
[8] Doucet, J., et al., Waste and Biomass Valorization, 5(1), 1-10, 2014.
[9] Farag, S., et al., Applied Thermal Engineering, 36(0), 360-369, 2012.
[10] Vanreppelen, K., et al., Chemical Engineering Journal, 172(2–3), 835-846, 2011.
[11] Max, P., T. Klaus, and W. Ronald, 2012.
[12] Zhang, Y., et al., Bioresource Technology, 127(0), 358-365, 2013.
[13] Farag, S., L. Kouisni, and J. Chaouki, Energy & Fuels, 28(2), 1406-1417, 2014.