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Bio-oil production via catalytic microwave co-pyrolysis of lignin and low density polyethylene using zinc modified lignin-based char as a catalyst

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ABSTRACT

In order to improve the product quality and make the process more sustainable, lignin-based char was used as a catalyst during microwave co-pyrolysis of lignin and low density polyethylene (LDPE). Lignin-based char modification using zinc transition metal proved to be beneficial by improving the porosity and selectiveness of the prepared catalyst. General selectivity of lignin-based char catalyst was observed to produce bio-oil with high selectivity of valued compounds. GC/MS analysis proved that the major chemical components of the bio-oil were hydrocarbons, ketones, alcohols, phenols and guaiacols(~70%). A central composite experimental design (CCD) was used to optimize the product yield and component composition. The optimum condition to produce the highest quantity and quality of bio-oil was 450 °C and 12.5% LDPE/lignin ratio. GC analysis of the syn-gas revealed that the valued compounds were H_2, CO and CH_4, the content of which was about 40%, 20% and 5%, respectively.

1. Introduction

In recent years there have been plenty investigations into the production of renewable energy sources. This has become a major concern as a result of increased awareness of the negative effects the continuous use of petroleum derived fuels and chemicals have on the environment [1]. With increased awareness by individuals and governments agencies around the world the technology used for producing renewable energy has been increasingly simplified. The simplification of the technology has shifted the focus to the variation of products that can be obtained from these sources. There are several sources of renewable energy; these may include solar, geothermal, hydro, wind and biomass. Out of all the sources mentioned biomass is the only source material that can be used to create solid, liquid or gas products [2]. Biomass can be converted to valued products through two pathways which are biological or thermochemical [3,4]. Biological pathway primarily involves the use of microorganisms that contains enzymes which convert the biomass into valued products [5]. The biological pathway is very delicate and highly restricted because these biological entities can only survive under specific conditions [6]. On the other hand, there is the thermo-chemical conversion; thermo-chemical conversion is comprised of several processes. Some of these process are combustion, torrefaction, gasification, and, pyrolysis. The difference between these processes is the relationship the biomass transformation has with the available oxygen. In the list from combustion to pyrolysis there is a gradual decrease in the amount of available oxygen during transformation [7]. However thermo-chemical conversion differs from biological conversion because it uses heat and pressure to break down complex bio-molecules into smaller fragments that are easier to manage and have more value [8]. Biomass pyrolysis refers to the thermal degradation process of organic compounds in the absence of oxygen to obtain bio-oil, syngas, and biochar, the converion of biomass to high value added fuels and chemicals via pyrolysis has received increasing attention in the past two decades [9–11].

Even though biomass is one of the most available sources for renewable energy, the specific material which should be used is a factor that should be considered. Out of all the possible sources of biomass the most abundant is lignocellulosic biomass. Lignocellulosic biomass is composed of primarily three major compounds that are cellulose, lignin, and hemicellulose [12]. Cellulose is generally the largest fraction, representing approximately 40 wt.% to 50 wt.% of the biomass, lignin is the second largest fraction that is approximately 16 wt.% to 33 wt.% depending on the feedstock source, and the hemicellulose portion occupies a majority of the remaining mass. Out of the three

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major components, lignin is the least understood and least used because of its molecular structure. There are many industrial sources of lignin that can be used to produce valued compounds; one source that has been considered comes from the paper and pulp industry. Annually about 400 million metric tons of paper is produced which leaves an excess amount of waste lignin that is used as low grade heating material [13]. Considering the high availability of this material there have been several investigations into its use as a fuel source [14,15]. For improved product quality and sustainability the addition of waste plastic material to the biomass during pyrolysis has been considered. This is a suitable material because it is rich with hydrocarbons and if not recycled it is one of the leading cause of environmental pollution. Annually about 100 million metric ton of waste plastic material is discarded [16]. Recently, co-pyrolysis of biomass with polymers for bio-based fuel and chemicals production has drawn considerable attention [17,18]

Microwave pyrolysis of biomass involves the process that biomass is converted to bio-oil, syngas and bio-char via microwave-assisted heating, in comparison with conventional pyrolysis, there are many advantages for microwave pyrolysis including energy efficiency due to no size reduction and drying, mild reaction condition, and higher quality of products [19,20]. The parameters of microwave biomass co-pyrolysis with polythelene have been established, there are several investigations that have identified general conditions for the production of valued compounds during microwave co-pyrolysis [21–23]. Most of the research today is focused on improving the bio-oil product while reducing the cost of production. In order to improve the bio-oil composition, zeolite catalyst is one of the primary catalysts that have been used to do so [24,25]. Zeolite catalysts have been used in the fuel and chemical industry for a long time but in today's reality it is necessary to discover other types of catalysts that are just as good and are sustainable. This has led to the investigation of the use of waste lignin material as a selective barrier. Lignin-based char is a porous material that can select desired compounds in the bio-oil. Bio-based catalyst materials have been the subject of recent investigations, one of the principal directives for the use of these catalyst is to reduce the cost of production for the desired compounds. Oregui [26] investigated magnetically activated carbon derived from various bio-mass sources, in their investigation they explained that the modified catalyst was able to produce high quality bio-oil with valued hydrocarbons, ketones and phenols. In this investigation recycled lignin based char was used, the selectivity of catalyst can be improved by modifying the base structure with transition metal incorporation. This is similar to the results obtained by several investigations where they explained that the transition metal modification of ZSM-5 catalyst was superior to pure ZSM-5 catalyst and gave better results [27,28]. This investigation was performed with the objective of testing the selectivity of recycled char as a catalyst for bio-oil/bio-fuel production. This will eventually lead to a cheaper and more sustainable ways to manufacture high quality bio-oil using renewable catalyst materials.

2. Materials and methods

2.1. Materials

The lignin used in this investigation was purchased from Tokyo chemical industry Co. LTD., in Japan, the second material which was used is the LDPE which was purchased from China Petro Co. The elemental analysis of these materials are shown in Table 1. The analysis of the elements inside of the lignin shows that it is primarily made up of carbon and oxygen with small amounts of sulphur and hydrogen. Dry Ash Free biomass was used in the elemental composition analysis and the oxygen content was determined by the difference.

Table 1
Elemental analysis of Lignin and LDPE.

Compound	Carbon%	Hydrogen%	Sulphur%	Oxygen%
Lignin	42.65	4.97	7.26	45.12
LDPE	84.98	14.94	0.00	0.08

The transition metal used for the modification was obtained in the form of a hydrated salt ($Zn(NO_3)_2{\cdot}6H_2O$) which was purchased from Sinopharm Chemical Reagent Co. Ltd. Zinc was chosen as the modification metal because in previous experiments it has been reported to be optimum for compound selectivity [29].

2.2. Catalyst preparation

The excessive wetness impregnation method was used to modify the lignin-based char [30]. Lignin-based char was created using microwave heating, lignin biomass was measured and placed inside the reaction flask; no microwave absorbent was added so that the resulting char would be as pure as possible. The atmosphere inside the reaction flask was purged with N_2 gas in order to create an anoxic environment. The microwave was then set at a maximum temperature of 550 °C and a retention time of 30 min. This extensive time was to ensure that complete pyrolysis had occurred and only quality bio-char was left behind. After the bio-char was created it was removed from the reaction flask and allowed to cool down to room temperature. Whenever lignin powder undergoes pyrolysis it tends to form large clumps that stick together. In order to create the modified catalyst these clumps of char were grounded into fine powder and then sieved through a fine mesh to ensure uniformity of the size. The lignin-based char powder was washed repeatedly with de-ionized water to remove any contaminants from its structure and also to open the pores. After washing it was dried in an oven at 105 °C for 15 h to remove any moisture. The zinc metal was integrated into the crystalline structure of the lignin-based char by first dissolving the zinc salt in an excess of de-ionized water. The lignin-based char was then added to the solution; using a magnetic stirrer it was thoroughly mixed for 6 h in a water bath that was maintained at 60 °C. The use of the transition metal was in a 5% ratio to the lignin-based char framework. After mixing in the water bath, the catalyst was separated from the excess de-ionized water using a vacuum filter; and then molded into 3 mm x 3 mm x 5 mm cylindrical shapes and was dried in an electric oven at 105 °C for 15 h at vacuum. After drying the modified catalyst was calcined in a tube furnace at 550 °C for 4 h [31]. Inside the tube furnace an anoxic atmosphere was maintained by purging the system with 99.99% pure nitrogen gas with a flow rate of 60 mL/min.

2.3. Experimental procedure

The schematic diagram of the microwave pyrolysis apparatus can be seen elsewhere [3,7]. The microwave pyrolysis system consisted of the following components: a 1000W, 2.45 GHz microwave cavity manufactured by Nanjing XianouTechnology Company (Nanjing, China), an infrared temperature sensor for temperature measurement, a 500 mL quartz flask inside the microwave oven into which the biomass feedstock was loaded, a packed bed reactor for the catalyst and a product cooling and collection system where the condensable liquid(bio-oil) was collected. The feedstock was weighed out on an electronic scale and placed inside the reaction flask. All the experimental feedstocks were co-pyrolysis (lignin/LDPE) and were in accordance with the experimental design that was produced by the central composite design software. The infrared sensor was connected to the quarts reactor via a vertical quartz tube that pointed to the center of the biomass feedstock; this infrared sensor is a 24 V DCWAHOME model: IS-900AW sensor with a temperature range of 0–900 °C ; and has an output power of 4–20 mA. The catalyst and modified catalyst were used *ex-situ*, the ratio of the amount of catalyst used was 5 wt.% of the amount of feedstock that would undergo pyrolysis. The catalyst was placed in a packed bed reactor that was also maintained at a temperature of 500 °C. In order to