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Hydrothermal conversion of biomass (*Xanthium strumarium*) to energetic materials and comparison with other thermochemical methods

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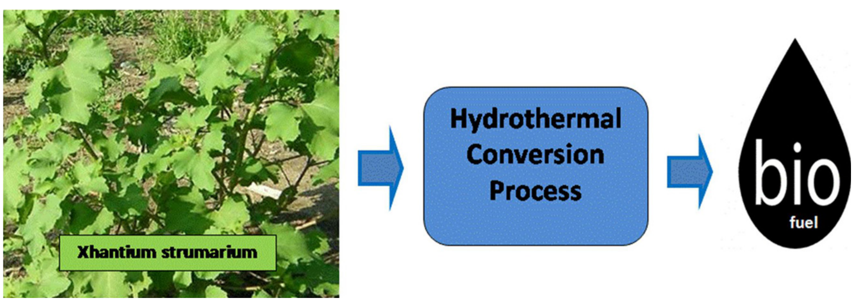
GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the biomass was converted into liquid and solid residues by using hydrothermal liquefaction method at 250, 300 and 350 °C with ($FeCl_3$, NaOH) and without catalyst. The resultant products were examined using GC–MS, FT-IR, ^1H NMR, SEM, and elemental analysis methods. According to the performed analyses, the highest liquid product yield (total bio-oil) was found to be 38.08% at 300 °C by using $FeCl_3$ as catalyst. In the experiments carried out at 350 °C, the highest HHV value was found to be 32.35 MJ kg^{-1} by using NaOH catalyst. The energy values of products obtained at the end of experiments were compared to the values obtained from pyrolysis and supercritical liquefaction method, and it was determined that the liquid products having higher level of energy value were achieved by using hydrothermal liquefaction method.

1. Introduction

The biomass is formed as a result of the conversion of carbon dioxide and water into macromolecular compounds within the plant such as lignin and cellulose by making use of photosynthesis [1]. The biomass is the 4th most frequently used energy source in the world, following the oil, charcoal, and natural gas. Besides that, 14% of the energy requirement is met by using biomass. The biomass has many advantages over the other energy sources. Some of them are that the biomass is a renewable energy sources that can be replaced within a short time by storing the solar energy, that the biomass is an environmental-friendly energy sources, and that it causes the formation of low levels of SO_x and NO_x thanks to its low sulfur and nitrogen content. Since the CO_2 is consumed in formation of biomass, it doesn't cause CO_2 release and it also contributes to increasing the air quality. Since the biomass can be easily obtained from the terrestrial and sea sources, it is more affordable than the other energy sources [2,3].

The biomass consists of polymers constituted by macromolecules incorporating C—C bonds. The main structure of polymers is constituted by the C—C bond, but there may also the bonds consisting of C—O,

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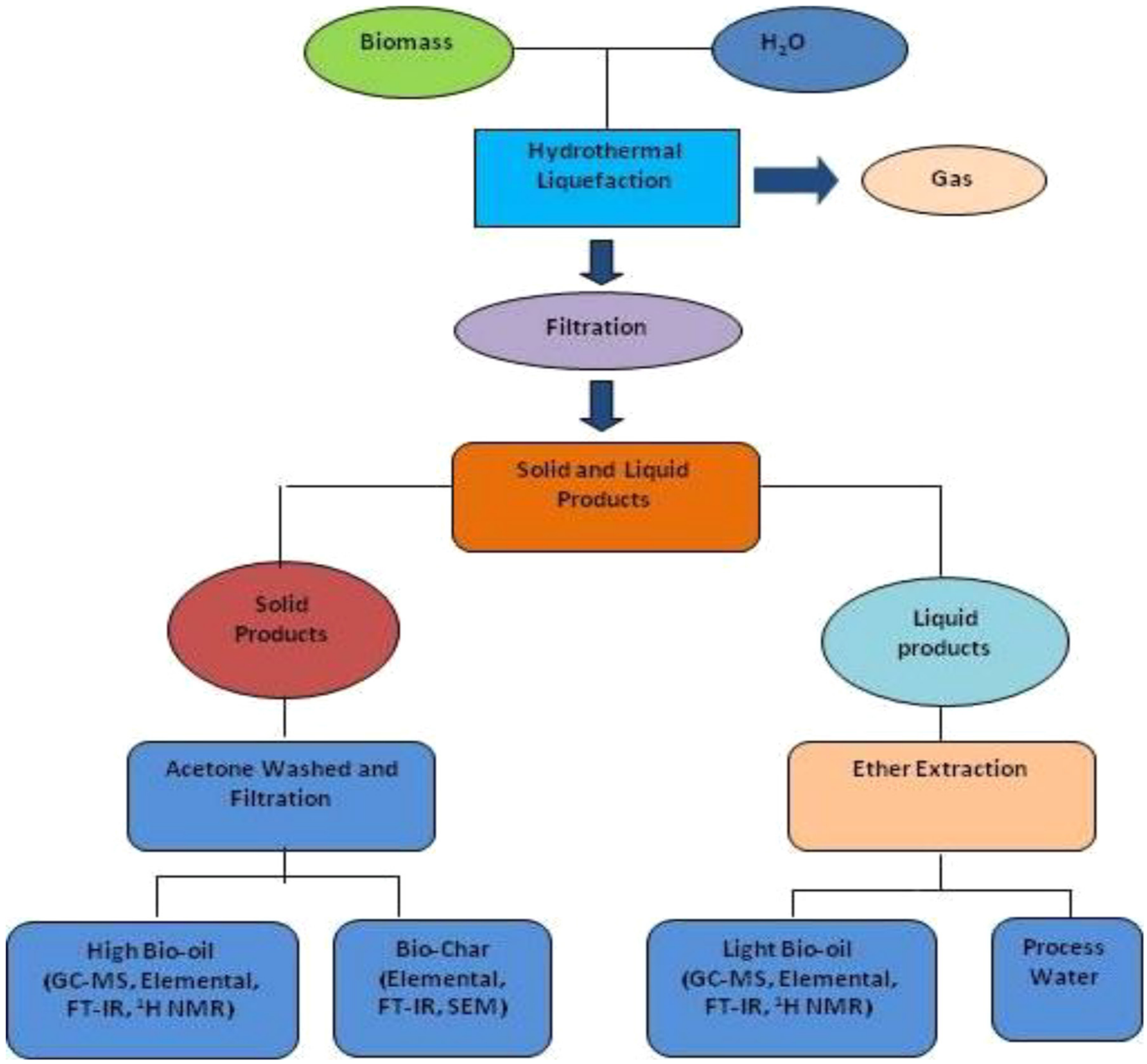

Fig. 1. The procedures for separation and analysis of hydrothermal liquefaction products.

C—H, C—N, C—S, and other elements. The polymers constituting the biomass are generally the macromolecular structures consisting of smaller units.

The hemicellulose is the heterogeneous polymer of pentose, hexose, and sugar acids. On the contrary with cellulose, the hemicelluloses are not chemically homogeneous. The hemicellulose is easily hydrolyzed with acids to self-forming monomers such as glucose, mannose, galactose, xylose, and arabinose. The hemicelluloses of hard biomasses such as tree mainly incorporate xylenes, whereas the hemicelluloses of softer biomasses include glucomannan. The xylenes included in the structure of different biomass sources (such as tree, weed, grain) have differences in their structures. Besides the xylenes, the hemicellulose xylose might also incorporate arabinose, glucuronic acid, acetic acid, ferulic acid, and p-coumaric acids. The polymerization degrees of xylenes, which are included in the structures of hard materials, are higher than the ones in structures of soft biomass sources.

Lignin is a tridimensional polymer, which consists of phenylpropane units connected to each other with C—O (ether) and C—C bonds and has very complex structures. The lignin is included in outer layers and contributes to the integrity of other polymers by reinforcing the stability and durability. In general, the soft biomasses have higher lignin concentration than harder ones. Lignin is classified into guaiacyl lignin and guaiacyl-syringyl lignin. Although the structure of lignin has been well-revealed, its chemical behavior is still not known exactly.

In meeting the energy requirements, the specific enthalpy and enthalpy density are very important in selecting the fuel accurately. In cases such as transportation vehicles, for which the fuel volume is very important, the enthalpy density is taken into consideration. Combusting 1 L of fuels having high level of enthalpy density generates higher heat levels and the selection is made upon this criterion. In order to obtain fuel with high level of enthalpy density from the biomass, the biomass should be converted into liquid products. The combustion is an exothermic reaction chain resulting in heat production and chemical conversion. During the combustion of biomass, the heat is generated in oxygen or air environment through the oxidation reactions of carbon, hydrogen, oxygen, and combustive sulfur and nitrogen compounds. This method is the most widely used method of generating heat from the biomass. The combustion is a low-cost method, mechanism of which is well-known. Converting the biomass into high enthalpy-density products instead of directly combusting it is very important for both of transportation and high-energy generation. The biomass is converted into products, which have high enthalpy density values, through combustion, pyrolysis, gasification, and liquefaction. In liquefaction methods, the water is also utilized, as well as the organic compounds such as ethanol, acetone, methanol, and butanol. Examining the study conditions, it can be seen that the studies using organic solvents and water differ in terms of temperature and pressure values.

Among the solvents used in liquefaction processes, the water is

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