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Hydrothermal treatment of biomass for energy and chemicals

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ABSTRACT

Pyrolysis oils are a product of fast pyrolysis or liquefaction of biomass. Those dark brown organic liquids are chemically a complex mixture and/or emulsion of water and degradation products of lignin (e.g. guaiacols, catechols, syringols, vanillins), cellulose (such as levoglucosan, dehydrated sugars, di-sugars, furancarboxaldehydes), and hemicellulose (such as acetic acid, formic acid). Composition strongly depends on conditions of pyrolysis process and great variety of biomass feedstock such as grasses and trees, and other sources of ligno-cellulosic material, derived from municipal waste, food processing wastes, forestry wastes and pulp and paper by-products. The present contribution will present an overview of current high pressure processes for treatment of biomass for production of energy and chemicals as well as the fundamental studies of phase equilibria of the systems pyrolysis oil/gas, which are crucial in biorefinery process design. In particular, phase equilibria of binary and ternary systems consisting of pyrolysis oil/supercritical fluid (pyrolysis oil/CO_2) and (pyrolysis oil/H_2) was studied in addition to the phase behavior of ternary systems of (pyrolysis oil/diesel/CO_2) and (pyrolysis oil/tail water/CO_2). These data are important for design of separation processes as well as for the application of these substances for commercial fuels.

1. Introduction

Biomass energy is derived from distinct energy sources like wood, agricultural residues, food waste and industrial waste [1]. The large amounts of waste biomass, which is a renewable resource, cause serious problems when not being processed. On the other hand, energy demand is still increasing and the use of fossil fuels still remains the principle energy source. This may consequence in the uncontrolled net global warming which may increase the number of extreme climate events [2]. Research on alternative sources of chemicals and fuel and production technologies has therefore attracted a great deal of attention [3].

Behind coal and oil, biomass fuels such as wood, herbaceous materials and agricultural by-products currently form the world's third largest primary energy resource [4,5]. There is a great advantage, conventional conversion of biomass to energy is considered to be carbon neutral [4,5]. Anyhow, harvesting biomass to produce energy may not be sustainable because it may result in reduced soil productivity by depletion of carbon and nutrients [6,7]. Waste products may be utilized by biomass pyrolysis [6,7].

Wood energy is derived both from direct use of harvested wood as a fuel and from wood waste streams. The largest source of energy from wood is pulping liquor or "black liquor", a waste product from processes of the pulp, paper and paperboard industry [6,7]. Waste energy is the second-largest source of biomass energy.

In recent years, hydrothermal conversion of biomass has attracted considerable attention since hydrothermal energy was accepted as a possible energy resource with a high potential. Initially, scientists were focusing mainly on the high temperature and pressure regime of materials processing since there was a serious omission in the knowledge on the solubility of several compounds, and also on the selection of an appropriate solvent [8].

In the field of energy, supercritical fluids have already been applied as a heat transfer media and a processing media in many energy production techniques. One of the earliest is "Residual Oil Supercritical Extraction" – ROSE process. Later supercritical fluids found application also in coal liquefaction and gasification, production of oil from oil shales and from oil sands, enhanced oil recovery, emulsion splitting procedure (oil–water) and enhanced gas recovery [9].

For design of any high pressure processes thermodynamic and transport properties have to be known [10], but still, literature data

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are scarce or even do not exist [11]. Therefore, development of new methods for investigation of thermodynamic data of binary systems of a compound in the presence of supercritical fluid at extreme conditions is essential due to the lack of the literature data. Available literature comprises expensive and time consuming methods [10]. Developing new methods for investigation of the above mentioned parameters is of a fundamental importance as interaction of substances with supercritical fluids at elevated pressures should be considered for the design of a feasible industrial process [12]. Nevertheless, solubility of the substance is the crucial parameter controlling economy of the process [11–13].

Also, to enable exploitation of several possible energy resources with high potential for production of energy and chemicals, parameters like diffusion coefficient, heat transfer coefficient, viscosity and interfacial tension should be considered [11–13].

The paper is organized as follows: Section 2 reviews different source of waste biomass and its energy potential. Advantages and disadvantages of the hydrothermal processes and the potentials of their use for the conversion of waste biomass into fuels and chemicals are discussed in Section 3. Section 4 presents fundamental studies of phase equilibria of the systems pyrolysis oil/gas, essential in biorefinery process design. Section 5 is a systematic review of techno-economic analyses for all the hydrothermal processes. Such a systematic review is up to our knowledge not yet available in the scientific literature. Future perspective of hydrothermal technology as a tool to obtain advanced materials is given with appropriate examples in Section 6. And finally, Section 7 concludes with possible scope for future research.

2. Source of waste biomass and its energy potential

As mentioned above, biomass takes the form of residual stalks, straw, leaves, roots, husk, nut or seed shells, waste wood and animal husbandry waste [5,14,15]. To maintain ecosystems services of nature useful to mankind, restriction of biomass production to degraded and currently fallow land is to be preferred [14]. Widely available, renewable, and virtually free, waste biomass is an important resource [5,14,15].

Globally, agriculture produces about large amounts of waste biomass every year. It is a great opportunity to convert this volume of biomass to an enormous amount of energy [16] and raw materials. The conversion of biomass to biofuels and biobased chemicals has attracted a lot of attention recently, largely due to the environmental and socio-economic problems associated with the use of fossil fuels. It is expected that agricultural biomass waste converted into energy products such as heat and steam, electricity, producer gas, synthetic fuel oil, charcoal, methane, ethanol, bio-diesel and methanol, will displace fossil fuel, reduce emissions of greenhouse gases and provide renewable energy to people in developing countries, which still lack access to electricity in the near future. Crops grown for energy could be produced in large quantities, just as food crops are [17,18]. While corn is currently the most widely used energy crop, native trees and grasses are likely to become the most popular in the future [17,18]. These perennial crops require less maintenance and fewer inputs than the annual row crops, consequently they are cheaper and more sustainable to produce.

Anyhow, calorific value of biomass is a strong function of its composition. For instance, dry woody biomass consists of cellulose, hemicelluloses, lignin and ash. By determining the calorific value and weight fraction of each constituent, its calorific value can be estimated. Direct combustion has been considered as the most frequently used and efficient way of deriving useful energy from biomass. Particle size significantly affects the rate of combustion and heat content per unit bulk volume of the fuel. Since biomass fuels burn principally in the gaseous state, the rate of combustion is proportional to the time required for heating and ignition of the volatile compounds. This turn is related to the exposed surface area per unit volume of fuel. The minimum particle size should be determined due to the fact that the total surface area of a given quantity of fuel is inversely proportional to the square of the average particle diameter. During the process the size of voids in the fire-bed is reduced as the particle size decreases. The point is reached where individual voids become so small that the resistance to passage of combustion air is unacceptable [19].

2.1. Municipal solid wastes (MSW)

Conversion of waste to energy is economically and socially sustainable and has strong potential to produce energy from communal and industrial waste, which are currently unused resources that need a further treatment to avoid the discharge of low concentrations of metals from landfills which may, however, cause environmental problems in the future [20–23]. In addition, it is necessary to integrate waste management procedures with waste quantity reduction [20–23]. Waste gasification is a good alternative of waste processing which benefits in energy recovery [22]. The investment cost of systems based on gasification does not exceed that of conventional WtE (Waste to Energy) plants. Moreover, it is even lower since the electric efficiencies of such systems can be up to 50% higher than conventional WtE plants. Consequently, the overall cost of such process is significantly reduced compared to the traditional waste destruction process [22].

2.2. Sludge

The amount of sludge, produced yearly by the treatment of municipal wastewater will increase considerably in the near future according to the forecasts because of the urbanization, industrialization, and growth in population [24,25]. Sludge management is an integral part of any modern municipal waste water treatment plant: it is important not to lose the nutrients in the sludge, to make use of its material and energy, and to dispose of it efficiently and sustainably [24,25].

Chemical, sewage sludge is a mixture of various organic and inorganic compounds. Several other elements, including heavy metals, are present in a variable content which are converted in the gaseous compounds as H_2S, NH_3, and HCl during gasification [26]. Since large part of these toxic pollutants originates from diffuse sources, the quality of the sludge will remain more or less the same. There is no doubt that the problem of sewage sludge is forecasted to grow and requires an appropriate treatment. A possible solution may be energy recovery from sewage sludge by the development and employing sustainable technologies in terms of cost and environmental impact [27]. Direct waste-to-energy incineration and complete combustion systems will require multi-step cleaning of the exhaust gas, to ensure no hazardous substances are released [28].

2.3. Other

The food industry produces a large number of residues and by-products, such as peelings and scraps from fruit and vegetables, food that does not meet quality control standards, pulp and fiber from sugar and starch extraction, filter sludge and coffee grounds, that can be used as biomass energy source. Oil palm is a multi-purpose plantation and it is also an intensive producer of biomass [27]. Bunches from oil palm tree are further used as feedstock for palm oil production in palm oil extraction process by means of screw type press. Bio-waste management and research related to innovative treatment methods is focused towards new techniques

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