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Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass

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ABSTRACT

Lignocellulosic biomass is a promising source of renewable energy and valuable chemicals. It is abundant in several forms which may be pyrolyzed to give gases, condensates and char. The condensed liquid obtained through pyrolysis is popularly called bio-oil from which valuable chemicals may be derived in a well defined manner. Chemically, this liquid is a complex mixture of simple organic, inorganic and macromolecular compounds formed through thermo-chemical breakdown of lignocellulosic biomass. High oxygen content is responsible for its low gross calorific value which renders it useless for fuel applications however; upgrading processes aimed at reducing oxygenates potentially increase its usage at par with fossil fuels. Fast and efficient analytical methods have revealed huge amount of informations from biomass and pyrolysis liquids hence a key component in organizing research in this area. Owing to the high compositional complexity and diversity in bio-oils originating from different sources, generalized analytical procedures are very difficult to formulate. However, tools of analytical chemistry have helped in understanding the underlying mechanisms involved in production and upgrading of bio-oils at molecular levels. With the possibility of commercial large scale production plants coming up in Europe, concerns with bio-oil quality, stability and upgrading rely strongly on analytical approaches. With this review we have tried to present outcomes of important research related to chemical analysis of bio-oils. The discussion is intended to summarize role of prominent analytical techniques in the chemical characterization of bio-oils. On this basis, optimum sample preparation strategies have also been proposed along with the rationale behind analysis with conclusions.

1. Introduction

Global energy requirements across all major segments rely on fossil fuels which is responsible for its fast depletion. Improving lifestyles, growing population and strong economic growth in the developing world has necessitated search of renewable sources of energy [1,2]. International Energy Agency has summarized overall global energy supplies, gross consumption across various sectors and anticipated demand in the future. It has also estimated the utilization of renewable and non-renewable fuels for electricity generation [3]. Worldwide, the transportation sector accounts for major energy requirement which is met through fossil fuels. Indian transport system expanding at 10% annually is considered one of the largest and heavily populated systems with serious fuel demands [4,5]. Power generation in US is largely achieved through natural gas whereas coal remains a key feedstock in Indian thermal power plants which meets nearly 65% of its total installed electrical capacity [2,5]. In addition to this, rapid economical and population growth of developing world (China, India, Latin America, Middle East and Russia) has crucial energy expectation. Limited petroleum reserves [6] and environmental concerns have necessitated the exploration of new sources of renewable energy.

Biomass is an abundant renewable source from which fuels can be obtained in relatively short span, reliable and eco-friendly manner [7,8]. It provides energy efficient fuels in the form of bioethanol and bio-diesel which makes up first generation biofuels. Bioethanol is generally produced from food grade agricultural biomass and used as additive in gasoline. Its use of up to 25% as gasoline blend is prevalent in the different parts of globe especially US and Brazil [9,10]. Bio-diesel on the contrary, is a common biofuel in Europe obtained from vegetable oils and animal fats. It is also used as diesel additive to reduce levels of particulates and toxic emissions (e.g. carbon monoxide and hydrocarbons) from vehicular exhausts [11–13].

Bio-oils are obtained through a single step thermo-chemical conversion of nearly all kinds of wood biomass into a chemically complex liquid product. An estimated increase of nearly four to seven folds in energy density is readily achieved during this process

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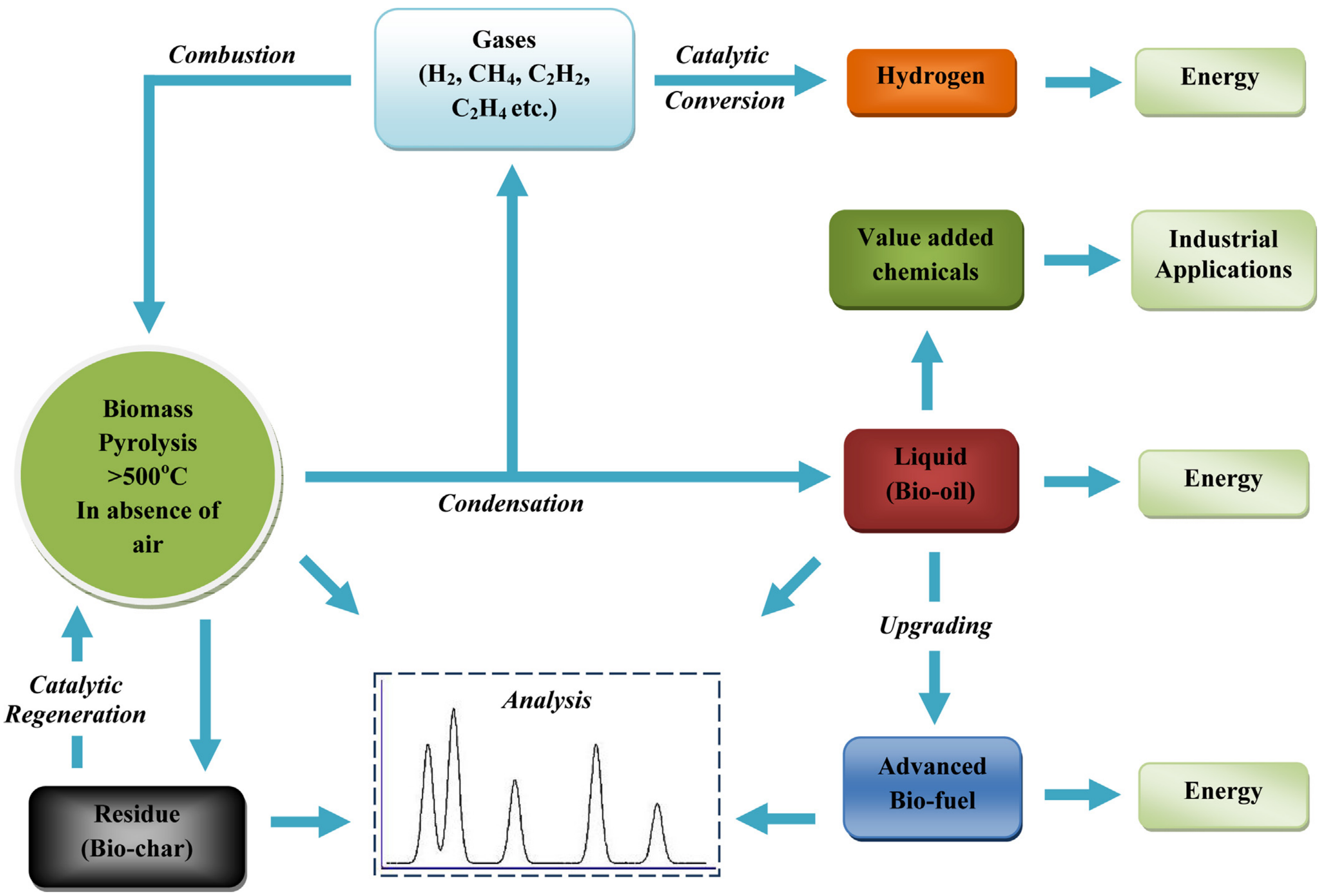

Fig. 1. A schematic pathway of biomass pyrolysis to yield bio-oil.

termed pyrolysis [14–16]. During past three decades, researchers across the globe have emphasized upon evolving bio-oils as a potential substitute of petroleum [17–19]. Bio-oil is a dark colored liquid comprising mixture of organic compounds that serves as mother liquor to variety of chemicals. Pyrolysis is the destructive distillation of dried biomass in a reactor at high temperatures [20–22]. Raw and unprocessed bio-oil on the basis of its gross calorific value may be employed as an alternative to the solid fuels (wood, coals etc.) used in boilers for power generation. It is a promising source of numerous value-added chemicals [23]. Considerable efforts are being continuously put in to develop upgrading strategies to transform it to engine fuel applications. Bio-oils are often termed '*clean*' compared to fossil fuels since they offer several ecological benefits [22].

Pyrolysis causes irreversible breakdown of organic matter at elevated temperatures in the absence of oxygen that brings tremendous change in the physico-chemical properties of feedstock leading to the formation of condensates. A schematic sketch of biomass pyrolysis process to produce bio-oil and its subsequent value addition is summarized in Fig. 1. The pyrolysis process of lignocellulosic biomass has been review by many researchers [24–31]. These reviews are highly informative, fundamental and encompass several aspects of pyrolysis process, reactor designing, process scale-up and commercialization under global perspectives. Mohan et al. detailed a comprehensive report on different types of pyrolysis and highlighted prerequisites for carrying out pyrolytic breakdown of wood biomass considering their varying chemical compositions [22]. Similarly, biomass pyrolysis methods have been reviewed and thoroughly described with mechanisms and kinetics of pyrolytic reactions and chemometrics [32].

Extensive research in this area reveals a high level of diversity in selecting biomass comprising agricultural and forest scrap such as barley straw and hulls [33], rice husk [34–36], wheat straw [37,38], corn (stalks, leaves and husks) [39,40], coconut and peanut shells [40], fruit bunches and pulps [41,42], waste furniture and wood (eucalyptus, pine etc.) [38,43–46], forage crops [47,48], tea waste [49], bagasse [40,50], sewage sludge [51], swine manure [52] and many more. Interestingly, waste plastic and printed circuit boards from used computers have also been utilized to produce pyrolysis oil [53,54]. Algae are rich source of energy due to higher photosynthetic efficiency than trees and therefore considered to possess high solar energy content. In order to achieve efficient carbon dioxide fixation, algal biomass has been efficiently utilized to produce bio-oils [55–58]. Essential parameters for algal biomass pyrolysis to extract valuable chemicals, bio-fuels and gases have been reviewed [59].

Bio-oils are obtained in fair yields (70–80% w/w) from almost all kinds of lignocellulosic biomass and their chemical compositions vary sharply according to the biomass [60]. Briefly, pyrolysis causes thermal cracking of naturally occurring biomolecules (cellulose, hemicelluloses, lignin etc.) in the biomass and converts them to simpler organic molecules. Other constituents of wood such as fats, mucilage, wax, alkaloids, terpenoids etc. are converted into smaller compounds and inorganic minerals are reduced to ash during this process. Bio-oils usually are dark colored, viscous and unstable liquids with considerable water content. Upon storage they undergo series of chemical reactions triggered by organic acids and intermediates in addition to the re-polymerization of reactive olefinic compounds [61,62]. Ageing also reduces bio-oil quality, increases its viscosity and ultimately leads to the separation of continuous