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Pyrolysis of *Jatropha Curcas* seed cake followed by optimization of liquid–liquid extraction procedure for the obtained bio-oil

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ABSTRACT

Lignocellulosic biomass is considered an abundant and renewable source to produce bio-oils with an objective of its value addition for fuels and chemicals. Upgrading strategies have immensely evolved as a result of ever progressing research in this field. Development of complete analytical protocol for bio-oil characterization at different stages of its production, storage, upgrading and during its use is essential for the purpose of its quality assurance and understanding. This report is aimed at developing a sample preparation procedure for bio-oils involving an extensive liquid–liquid extraction approach. Bio-oil obtained after slow pyrolysis of *Jatropha Curcas* seed cake was phase separated and subjected to solvent extraction. Various solvents were screened for their extraction capabilities towards available organic compounds of all functional group in the bio-oil. Ethyl acetate, dichloromethane, carbon tetrachloride, diethyl ether, benzene, cyclohexane and hexane were employed for extraction of aqueous phase under similar conditions. Recoveries of compounds containing varying functional groups indicated ethyl acetate and dichloromethane as optimum among all other solvents. During the extraction, partitioning of compounds between bio-oil phase and solvent occurred largely on the basis of polarity. Acidic and basic organic compounds present in the aqueous phase were determined after adjusting the pH of samples followed by dichloromethane extraction. A comprehensive detail of the extracted chemicals and their classification has been provided. The identification was carried out qualitatively with GC–MS and derivatization of polar chemicals was also carried out before analysis. These experiments compare the efficacy of various organic solvents for extracting diverse bio-oil pyrolytic products. The findings are important in ascertaining usefulness of organic solvents towards enrichment of available bio-oil chemical groups. The information may be either utilized for characterization purposes or their monitoring during upgrading process.

1. Introduction

Energy requirements across all the sectors have been continuously increasing owing to the improving lifestyles and rapid population growths especially in developing countries. Extensive utilization of fossil fuels chiefly in the form of coal, oils, and gases is widespread to meet this energy requirement. Diminishing petroleum reserves has necessitated the increased refining of heavy and sour crudes across the globe. Over the past several decades, environmental pollution has emerged as a consequence of petroleum consumption particularly in transportation, power generation and industrial revolution. It has necessitated the exploration of alternative, new and renewable sources of energy [1]. In the contemporary context, conversion of biomass to biofuels and chemicals through thermal degradation in an integrated refinery appears to be a promising approach. Lignocellulosic biomass is an abundant and renewable source from which fuels and chemicals may be obtained in reasonable yields, and ecological and environmentally friendly manner [2,3].

Pyrolysis of wood biomass was prevalent in ancient societies where tars and condensates were used for various applications (embalming fluids, sterilizing properties, deodorizer, preservative,

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flavours, fertilizer and source of essential oils & bio-pesticides) [4]. There are several ways of converting lignocellulosic biomass into *bio-oils* also called *pyrolysis oils*. Pyrolysis is a widely adopted process for the thermal breakdown of biomass feedstocks in the absence of oxygen which leads to the thermo-chemical fragmentation of plant bio-macromolecules. It is a complex sequence that involves fragmentation of larger macromolecules into smaller compounds of which reactive ones rearrange to give stable molecules. The pyrolysis is essentially time dependent (fast, slow and flash) and yields gaseous, liquid, and solid products [5,6]. Utilization of bio-oils remained restricted for quite some time due to unavailability of efficient procedures of handling upgrading. As the researchers realized tremendous prospect of bio-oil utilization and eventual upgrading into fuel and chemicals, several limitations associated with its use, handling, storage, transportation and refining have been significantly surmounted. Considerable efforts are being continuously put in to develop and improve the upgrading strategies to transform bio-oils into prospective engine fuel applications and chemicals [7–12].

The quality and quantity of bio-oil, char, and gases is largely governed by the nature of biomass feedstock. Since the pyrolysis process is time and temperature dependent, the reaction kinetics, heat transfer, thermal stability and phase separation of formed chemicals determine the overall product distributions. [13]. Wide ranging biomass comprising agricultural and forest scrap such as barley straw and hulls, rice husk, wheat straw, corn plant (stalks, leaves, and husks), coconut shells, peanut shells, fruit pulps, woods (waste furniture, eucalyptus, pine, etc.), forage crops, tea waste, bagasse, and many more have been used to produce bio-oils [14,15]. Lignocellulosic biomass typically contains cellulose, hemicellulose, and lignin in addition to other minor constituents as fats, mucilage, wax, alkaloids, terpenoids etc [16]. Pyrolysis of these biopolymers generates considerable amount of oxygen (in the form of oxygenated organics) in bio-oils which distinguishes it from fossil fuels. It is also responsible for its low heating value. Mechanistically, cellulose thermal degradation produces levoglucosan, levoglucosenone, furfural, substituted furans, several aldehydes and ketones. Hemicellulose pyrolysis leads to the formation of volatile organic compounds and smaller amounts of levoglucosan. Deacetylation of hemicellulose leads to the formation of acetic acid which is responsible for acidic nature of bio-oils. Lignin is a major source of phenol containing species in bio-oils formed as a result of its thermal decomposition. Phenols and methoxyphenols (of which monolignols such as guaiacol and syringol) are prominent products which are produced in this way.

Pervasive research in the area of bio-oil production has led to the optimization of several processes and improved our understanding at the molecular level. Briefly, bio-oil is a dark coloured liquid comprising complex mixture of varied organic compounds. The complex composition of bio-oils is described as multi-phasic due to presence of char particles, waxy materials, aqueous droplets, droplets of different nature, and micelles formed of heavy compounds in a matrix of holocellulose derived compounds and water [17]. The prospects of bio-oil for being used as starting material for several applications diminish due to deterioration of its quality. Loss of volatile compounds leads to increase in its viscosity and molecular weight as a result of which storage, transport and use of bio-oils becomes challenging. Understanding the mechanism of chemical and physical aging is fundamental to address the associated limitations with its use. A detailed discussion of the probable reactions which take place in such an extremely complex matrix is beyond the scope of this paper. However, there are several organic reactions which have been proposed and probably occur to cause ageing of bio-oils at higher storage temperatures. Some examples include esterification of organic acids with alcohols and olefins; formation of germinal diols from aldehydes/ketones and water; hemiacetals/acetals from aldehydes/ketones and alcohols. Besides, several other organic reactions (oxidation, hydrolysis, substitution, elimination and rearrangements) also occur due to the presence of highly reactive compounds such as acids, aldehydes, ketones, olefins and other reactive intermediates. It imparts instability to bio-oils which eventually leads to gradual change in the phases. Presence of organic acids remains the sole reason behind bio-oil acidity for which the pH generally ranges between 2 and 4 [18,19].

Engineering solutions have progressed for the production of bio-oils followed by development of several efficient upgrading strategies. Analytical tools have enormously contributed towards understanding the composition of produced and upgraded bio-oils and isolation of selected chemical families [20]. Upgrading of crude bio-oils is a series of processes involved to overcome limitations associated with its use and extremely essential for its scale-up production and refining processes. The key objective of upgrading is the removal of free organic acids (formic, acetic, propionic acid, etc.) through esterification. Catalytic upgrading has been widely accepted to value add bio-oils [21–25]. Hydrotreatment of these liquids through ruthenium over carbon catalyst has been reported to yield around 65% product [26]. Bio-oil fractions have also been attempted for blending with bio-diesel and used as petroleum additive for transportation [27]. Several aspects of hydro-deoxygenation and zeolite cracking involving catalyst development and their performance evaluation have been reviewed [28]. Careful analytical studies have been executed from time to time aiming at revealing valuable insights of pyrolysis and upgrading processes [29]. Bio-oils have been largely characterized by several analytical techniques of which gas chromatography (GC) equipped with several detectors as flame ionization (FID), mass spectrometer (GC–MS) and multidimensional gas chromatograph coupled to time of flight based mass spectrometers (GCxGC-TOFMS) are important [30–32]. Role of various analytical techniques in bio-oil characterization have been reviewed [14,33]. It can be seen from the enormous literature reports that emission/absorption/fluorescence in addition to mass spectrometry based detection techniques are highly sensitive and widespread in this area. GC–MS being a versatile system has helped in understanding bio-oils more than any other analytical technique.

Sample preparation is an imperative part of almost all forms of chemical analysis and considered time consuming and labour intensive. In bio-oil analysis, it plays a major role in the isolation and characterization of every chemical family. During the initial years of research into this area, filtration, centrifugation and phase separation by water addition was reported [34]. Complex nature of bio-oils often restricts the application of limited set of protocols for its complete sample preparation. Several approaches for bio-oil sample preparation are available in the literature that includes solid-phase extraction (SPE), ion-exchange and size exclusion chromatography [35] and gel permeation chromatography [36]. Liquid–liquid extraction (LLE) has been used for fractionation of bio-oils obtained from several lignocellulosic biomass feedstocks. Various organic solvents have been reported in addition to the ionization suppression through pH manipulation and soxhlet extraction. Authors have used diethyl ether, acetone and ethyl acetate to recover chemicals form pyrolysis liquids [37]. Oasmaa et al. determined chemical classes of bio-oil responsible for imparting acidity to the bio-oil by simply preparing water soluble and insoluble (i.e. dichloromethane or hexane soluble) and analyzing them further [38]. An elaborated fractionation of bio-oils was proposed in which bio-oil was subjected to toluene, methanol, water, diethyl ether and dichloromethane (DCM) extraction [39]. We herein report comprehensive optimization of bio-oil fractionation through LLE followed by GC–MS characterization. The study is original and novel in terms of reporting the optimized solvent extraction procedure for bio-oil obtained from *Jatropha Curcas*