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Extraction of cardanol and phenol from bio-oils obtained through vacuum pyrolysis of biomass using supercritical fluid extraction

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ABSTRACT

The feasibility of extraction of phenol rich oil from the bio-oils obtained through pyrolysis of cashew nut shells and sugarcane bagasse is studied. The extraction rate of phenol rich oil using CO_2 as a supercritical fluid is discussed. Operating parameters are optimized for the maximum concentration of phenol and cardanol. Higher yield of oil (50% by weight) along with higher concentration of phenols and cardanol by present method is found encouraging. The experiments were conducted in the pressure range of 120–300 bar, the temperature range of 303–333 K and the mass flow rate range of 0.7–1.2 kg/h. The process parameters are optimized to maximize the yield of extracts and its contents of phenols and substituted phenols from sugarcane bagasse pyrolysis oil. The oil samples obtained at various operating parameters are analyzed by Gas Chromatograph–Mass Spectroscopy (GC–MS) and Fourier Transform Infra-Red Spectroscopy (FTIR).

1. Introduction

Biomass has been used as a source of food, fodder, fertilizer, feedstock and fuel, perhaps since the early development of mankind. The term biomass is very generic, which refers to any organic material formed by virtue of photosynthesis, directly or indirectly.

Conventionally, all these biomasses have been used for extraction of energy and chemicals through various routes and processes – broadly classified as bio-chemical and thermochemical processes. Fermentation is used to convert cellulosic compounds to ethanol; distillation has been traditionally used to convert the ligno-cellulosic wood into methanol. Bio-gasification route is applied for biodegradable materials to produce biogas, and thermal gasification is being used to convert dry ligno-cellulosic compounds to produce gas. Today, pyrolysis is fast gaining importance as an effective method of converting biomass into energy and variety of chemicals through the thermochemical route.

Pyrolysis plays an important role in any thermochemical conversion of biomass. It is referred to as carbonization, liquefaction or gasification depending upon whether the desired product is solid char, liquid fuel/chemical or gaseous fuel. This product distribution may be altered by manipulating the operating parameters such as, heating rate, temperature, residence time, etc. Today, the term 'pyrolysis' is generally used to describe processes in which preferred products are liquids that may be used as fuel or chemical. Bio-oil, obtained through vacuum pyrolysis, is typically dark brown in color with a distinctive pungent smell. This liquid contains several chemicals in different proportions. The applications of bio-oil are well reported in the literature [1]. On an average pyrolysis liquid obtained through various biomasses contains about 10–20% water, 15–30% lignin fragments, 10–20% aldehydes, 10–15% carboxylic acids, 5–10% carbohydrates, 2–5% phenols and traces of furfurals, alcohols and ketones [2].

The most significant products from phenol are phenolic resins, which are used as a raw material for laminate industries and manufacturing of special chemicals. The annual demand of phenol is more than 120,000 tonnes in Indian context and it increases at the rate of 8% p.a. [3]. The raw materials for phenol manufacturing are benzene and propylene. There is likely to be a shortage of both benzene and propylene in local market. Moreover, the chemical process of manufacturing phenol ends up with large amount of waste-water containing significant amount of phenols which is of environment concern. Hence, there is a strong requirement for an alternative, which can reduce the consumption of petro-based phenols and also be environment friendly. Within ten years DuPont hopes to derive 25% of its chemicals from renewable sources, and the prestigious US National Research Council predicts 50% of US

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fuels and over 90% of US organic chemicals will come from renewable sources [4].

Phenol extraction from biomass is well reported in the literature. Several U.S. patents also describe the extraction of phenol from biomass with different processes. U.S. patent 4,605,790 discloses the phenol extraction from mixed phenols obtained from ligno-cellulosic biomass by isomerisation, demethylation, and polymerisation processes [5]. A process of selective adsorption of biomass derived phenols using metal oxide has been patented (U.S. patent: 6,719,908) by Hames [6].

Phenols are also extracted from the bio-oil obtained through pyrolysis route. Fractionation of this recovers valuable fractions consisting of a phenolic fraction, organic acids and solid residue. Phenols are separated from this mixture by treating it with base like sodium hydroxide and subsequently by solvent extraction [7]. The solvent extraction is generally employed to get higher concentration of phenols from this oil. However, the solvent extraction has a serious problem of elimination of polluting organic solvent from the extract.

Meanwhile, supercritical fluid extraction (SFE) emerges as a new technology for the extraction of chemicals from plant material [8]. This process has an immediate advantage over traditional extraction processes like solvent extraction and steam distillation by virtue of elimination of polluting organic solvent from the extract and continuous modulation of solvent power of supercritical fluid [9]. In the past two decades, much attention has been directed to the use of SFE using supercritical CO_2 (solvent) in the food, flavour, fragrance and pharmaceutical industries. Supercritical carbon dioxide (SC-CO_2) extraction can be performed at lower temperatures and its solvent power can be fine tuned by choosing suitable operating condition to exclude the extraction of desirable/undesirable compounds.

Cashew nut shells and sugarcane bagasse, upon pyrolysis, give phenol rich oil along with other chemical components [10,11]. Smith et al. [12] reported that cashew nut shell liquid (CNSL) contains about 29 mol% cardols, and 21 mol% cardanols (group of phenols). The selective separation of such phenols and substituted phenols has been demonstrated using SFE in subsequent sections. The present study deals with the extraction of chemicals from the liquid products, obtained through pyrolysis of biomass. One such chemical, obtained from ligno-cellulosic biomass having the potential to replace petro-derived chemicals is 'phenol' (phenols, substituted phenols and their derivatives).

Supercritical carbon dioxide extraction of phenols from sugarcane bagasse pyrolysis oil and cashew nut shell liquid eliminates the use of hazardous solvents. SC-CO_2 is extremely 'green' solvent since by reducing the pressure it is returned to its former gaseous state and can be readily separated from the product and recycled. This study explores the use of SFE for selective extraction of cardanol and phenols, in particular from the CNSL, making this oil an attractive commercial product. This study illustrates the new methodology for CNSL extraction by supercritical fluid extraction route.

2. Details of experimental work

2.1. Biomass selection

Lignin content in biomass pauses a high resistance to mass transfer. However, upon thermal degradation of the ligno-cellulosic compounds, one is able to get a complex bio-oil composed of many compounds – a major fraction of which is a group of phenols. Sugarcane bagasse is one such biomass, which is available in abundance worldwide and in India in particular and is selected for the present study. It is a residue left after juice extraction. It may be noted that about 4 million hectares of land is under sugar cultivation in India. The production of sugarcane in the recent years has fluctuated between 230 and 300 million tonnes [13]. Besides India and Brazil, China, Thailand, Pakistan, Mexico and Australia are major contributors to world production of sugarcane. Das et al. [10] have studied sugarcane bagasse pyrolysis extensively including the effect of pretreatment.

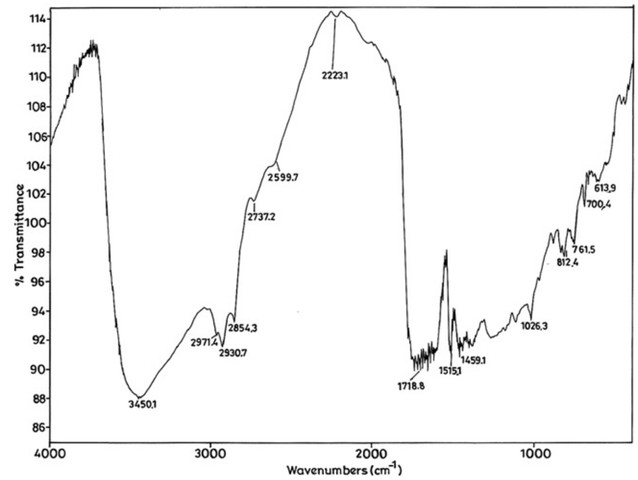

Fig. 1. FTIR spectra of extract obtained through SFE of bagasse pyrolysis oil (SBPO) at 300 bar.

The other biomasses selected for study are cashew nut shells, which have a naturally existing pericarp fluid, which is reported to be about 40% by weight of the shell. A major fraction of the fluid is known to be anacardic acid, which when decarboxylated gives a large aliphatic straight chain (15 carbon atoms) and a hydroxyl group attached to it on one end [14,15]. The potential application of this is well documented. Here again it is important to note that India is the largest producer and processor of cashews in the world. In India cashew cultivation covers a total area of about 0.77 million hectares of land. The average productivity/hectare is 760 kg. The world production of cashew nut kernel was 907,000 metric tonnes in 1998 [16,17]. Cashew Nut Shell (CNS) obtained from Pondichery, a Union Territory in southern part on India, has been used in the present study.

2.2. Solvent selection

The most desirable super critical fluid (SCF) solvent for extraction of natural products is carbon dioxide (CO_2). It is inert, inexpensive, easily available, odorless, tasteless, and generally regarded

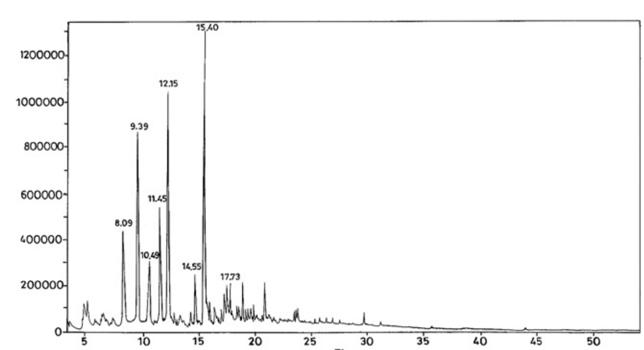

Fig. 2. GC–MS spectra of extract obtained through SFE of bagasse pyrolysis oil (SBPO) at 300 bar.