SELECTIVE EXTRACTION OF PHENOLS FROM SUGARCANE BAGASSE PYROLYSIS OIL

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Abstract

This paper illustrates the methodology for sugarcane bagasse oil (SBO) extraction by supercritical fluid extraction (SCFE) route using carbon dioxide as a supercritical fluid. This experimental work was conducted to identify the best process conditions to maximize the yield of extracts and its contents of phenols and substituted phenols. The experiments were repeated for the SBO obtained through pyrolysis route both from leached and unleached sugarcane bagasse. The experiments were conducted in the pressure range of 120 to 300 bar, temperature range of 303 K to 333 K and mass flow rate range of 0.7 to 1.2 kg/hr. The chemical compositions of the extracts were identified using Gas chromatography Mass spectroscopy (GC-MS) and Fourier Transform Infra Red (FT-IR) spectroscopy. The presence of these in-situ phenols can be advantageous. The phenols and substituted phenols, so extracted, may be used as natural phenols for making phenol-formaldehyde resins, which reduces the dependence on petro-based phenols for resin manufacturing.

Key words: Supercritical, Sugarcane bagasse, Phenol.

Introduction

Bio oil, obtained through vacuum pyrolysis, is typically dark brown in colour 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]. One such application is the recovery of chemicals such as phenols, resin, agri-chemicals, fertilizers and emission control agents. On an average pyrolysis liquid obtained through various biomass contains about 10 to 20 % water, 15-30% lignin fragments, 10-20% aldehydes, 10-15% carboxylic acids, 5 to 10% carbohydrates, 2-5 % phenols and traces of furfurals, alcohols and ketons [2]. This in-situ natural phenol can be used for resin preparations. However, the presence of carboxylic acid puts a limit on direct use of bio-oils for such applications. Cashewnut shells and sugarcane bagasse, upon pyrolysis, give phenol rich oil along with other chemical components [3]. The selective separation of phenols and substituted phenols has been demonstrated using SCFE in subsequent sections.

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 120000 tonnes in Indian context and it increases at the rate of 8% p.a. [4]. The raw materials for phenol manufacturing are benzene and propylene. There is likely to be 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 the alternative, which can reduce the consumption of petro-based phenols and 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 fuels and over 90% of US organic chemicals will come from renewable sources by the end of this century [5]. Natural phenols can be extracted from the sugarcane bagasse pyrolysis oil along with char as the by-product.

Sugarcane is one of the important crops grown in more than 100 countries. The total area under cultivation is about 32 million acres producing more than 800 million tones of sugarcane. India is the second largest producer of sugarcane next to Brazil with 4.09 million ha of land under cultivation producing about 283 million tones of sugarcane every year. The average yield is 69 tones/ha. The sugarcane bagasse, the residue left after crushing sugarcane, is about 50% of the weight of sugarcane. Hence, there is a strong potential for the oil extraction from sugarcane bagasse for industrial applications. Supercritical carbon dioxide (SC-CO_2) extraction of phenols from sugarcane bagasse pyrolysis oil 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. The residue leftover after phenol extraction can be used as a fuel.

Methods and Material

About 2 kg of the sugarcane bagasse (with approximately 50% moisture content) was collected and dried in an oven at a temperature of 400 K for 3 to 4 hrs. The dried sugarcane bagasse was ground using kitchen grinder so that it can pass through 14-mesh sieve. They were then packed in the airtight polythene bags so that it would not absorb moisture. It was observe that the yield of dried sugarcane bagasse was 50% (by weight) on the basis of original wet bagasse.

Water leached sugarcane bagasse samples were prepared according to the methodology suggested by Das [6]. About 140 g of dried bagasse powder (mesh size 14) was added in 1600 ml of water. The mixture was stirred. This water leaching was carried out for 24 hours. After that the leached bagasse was washed with excess distilled water repetitively till the wash-water remained neutral. The water- leached bagasse was then again placed in an oven and heated at 380 K for about 10 hours. This oven-dried bagasse was then packed in an airtight polythene bag.

Experimental Programme

Pyrolysis of sugarcane bagasse

The pyrolysis of the leached and unleached bagasse samples was carried out in the pyrolysis reactor. About 150 gram of the bagasse sample was placed in a reactor. The pyrolysis of these samples was carried out at a vacuum of 720 mm of Hg and at a temperature of 773 K as suggested by Subbarayudu [7]. The volatiles were condensed in the condensing train consisting of five glass bottles. The volatiles condensed in first two bottles of the condensing train were collected for the further study. The rest of three bottles consist of aqueous fraction.

Supercritical fluid extraction of sugarcane bagasse oil

The bagasse oil collected through pyrolysis reactor was used as a feed material. About 100 gram of bagasse oil was kept in the extractor of SCFE experimental set-up. The experimental set up consists of a carbon dioxide cylinder, a pre-cooler, a positive displacement pump, a needle valve, a separator and a pre-heater. Carbon dioxide from the cylinder passes through a pre-cooler, a positive displacement pump, and a pre-heater before it enters the bottom of the extraction vessel. (The extraction vessel is maintained at a predefined temperature). The flow of carbon dioxide is controlled by a needle valve and is measured by a gas flow meter with an accuracy of ±0.01 kg/h. A variable frequency drive pump controls the pressure in the vessel to an accuracy of ± 0.1 bar. Extracted oil is recovered by expansion of the loaded solvent stream to ambient pressure in a glass separator. Extract is collected at a fixed time interval of 30 minutes (cumulatively) by closing the needle valve. This extract is then weighed. The needle valve is then opened and extraction process continues for the next interval. Runs have been carried out for six hours at the pressures of 120 and 300 bar. The extract of each run is analyzed for Gas Chromatograph Mass Spectroscopy (GC-MS) and Fourier Transform Infra-Red Spectroscopy (FTIR).

Chemical Characterisation

The fractions of supercritically extracted sugarcane bagasse (SC-SBO) oil obtained at different operating parameters of SCFE have analysed by GC/MS and FT-IR. The GC/MS analysis was done using a Hewlett Packard 5890 A. GC/MS system with a 30 m X 0.25 mm ID-capillary column coated with polysiloxane. The initial oven temperature of GC was kept at 100^{o} C for two minutes and then programmed to increase at a rate of 10^{o} C / min to 250^{o} C. Afterwards, it was increased at a rate of 30^{o} C/ min up to 280^{o} C. Helium was used as a carrier gas with a flow rate of 0.7 ml/min. The ratio of mass to charge (m/z) was used to identify the most probable fragments of the components elucidated. The percentage area of the peak identified by GC gave the relative concentration of the components present in the given fractions.

Figure 1 shows the IR spectrum of SC-SBO. The bands observed at 1026, 1290,1459,1515 and 1718 cm^{-1} are the characteristic peaks of bagasse oil. The band at 1718 cm^{-1} is assigned to aromatic benzene ring vibrations. The band present at 1459 cm^{-1} is due to the methoxy CH3 group. The band at 1290 cm^{-1} is attributed to the C–O stretching of the phenol. The band at 1026 cm^{-1} is assigned to the C–O stretching in secondary alcohol.

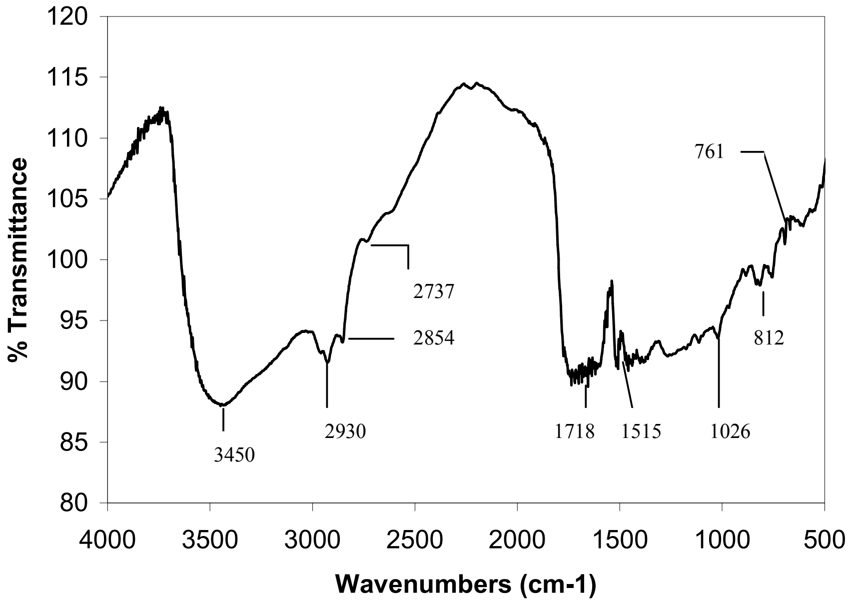

Figure 1 FT-IR Spectra of Sugarcane Bagasse oil obtained through SCFE

Results and discussion

The oil obtained at various operating parameters have been analysed for chemical compositions. The oil were analysed for GC-MS and FTIR. GC-MS helps in identifying the main components present in the SC-SBO along with their retention time. Mass spectra, through the molecular weight, help in identifying the component present in the SC-SBO. Table 1 shows the main components present in SC-SBO obtained at various operating parameters.

The studies on vacuum pyrolysis of unleached sugarcane bagasse suggest that the oil yield is approximately 20 % on the basis of weight of oven dried sugarcane bagasse and same has increased up to 40% on weight basis for the water leached sugarcane bagasse. However, considering the mass loss during leaching, the percentage yield of pyrolysis oil from both leached and unleached sugarcane bagasse on original weight basis was found same. Table 1 shows the area percentage of major phenol and substituted phenol peaks identified by GC/MS at different operating parameters in the SC-SBO obtained through SCFE from both leached and unleached sugarcane bagasse pyrolysis oil. . It was also found that the phenol and substituted phenol concentration in oil extracted by SCFE with unleached bagasse was more than that of leached bagasse oil. The concentration of phenol and substituted phenol is observed higher at higher operating pressure. Few more observations from GC-MS studies of sugarcane bagasse oil obtained through different routes is as under:

1. The number of components extracted from leached bagasse by pyrolysis is more.
2. The chemical composition of the oil from sugarcane bagasse using SCFE depends on the operating parameters.

3. The oil obtained through SCFE route is phenol rich. The concentration of phenol increases with increase in extraction pressure.
4. The oil obtained through SCFE route is free from all acidic and alcoholic components. It is due to the fact that CO_2 is used as the solvent SCFE process, which is non-polar and hence the solubility of highly polar substances like acids and alcohols in SC-CO_2 is negligible.
5. The absence of alkane and pthalate in the bagasse oil obtained through SCFE route is noteworthy. Alkanes and pthalates are higher molecular weight components. The solubility of components in SC-CO_2 decreases with the molecular weight.
6. Aldehyde and ketons are less polar substances and hence their solubility in SC-CO_2 is also moderate.

Stability characteristics of sugarcane bagasse oil

Figure 2 shows the viscosity variations with time for sugarcane bagasse oil obtained through different routes. The viscosity and its variation over time for SC-SBO has been compared with the same obtained through pyrolysis route [6]. It is observed that the viscosity of SBO obtained through SCFE route is the least. It is interesting to note here that the variation of viscosity with time in this SBO is very less. This is attributed to absence of highly polar fractions and acidic groups in SBO obtained through SCFE route. It clearly indicated that the oil obtained in this work is well stable and hence can be stored for longer period without much deviation in its physical properties.

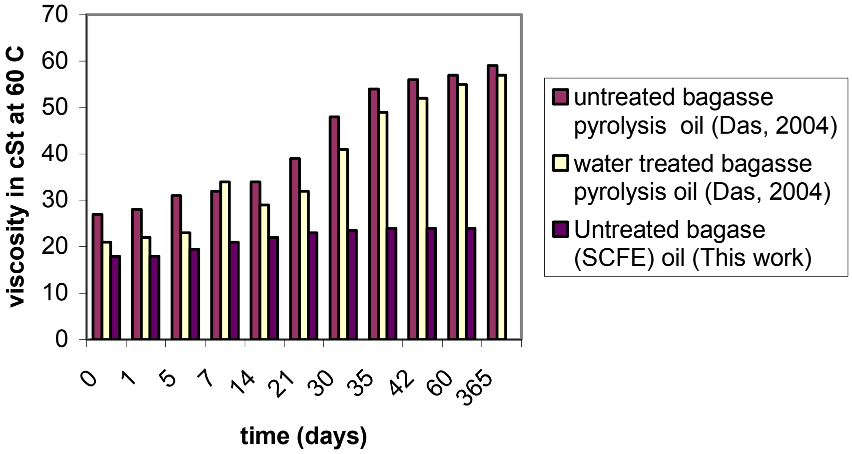

Figure 2 Variation of viscosity of SBO

Table 1 Concentration of phenol and substituted phenols in SC-SBO obtained at different operating parameters through GC-MS

	SC-SBO^U 300 bar	SC-SBO^U 125 bar	SC-SBO ^{L} 300 bar	SC-SBO^L 125 bar
Phenol	15.78	8.99	10.77	10.57
2-methyl-phenol	5.86	2.42	0.60	1.58
3-methyl-phenol	13.86	7.99	9.66	6.52
2,4-dimethyl-phenol	3.14	2.14	1.74	1.37
4-ethyl-phenol	26.79	12.97	10.08	7.54
2,4,6-trimethyl-phenol	1.29	-	-	-
3-(1-methylethyl)-phenol	1.71	-	-	-
4-ethyl-2-methoxy-phenol	1.34	-	3.18	-
2,6-dimethoxy-phenol	1.45	2.34	1.99	2.23
Total Phenols (Including substituted phenols)	**71.22**	**36.85**	**38.02**	**29.81**

^{U} Unleached bagasse ^{L} Leached bagasse

(Numbers in the table indicate the area percentage of identified peaks by GC-MS)

Conclusion

The effect of operating parameters on the extraction of SBO shows that the pressure and solvent flow rate significantly affects the yield of extract. The maximum yield (15%) of supercritically extracted sugarcane bagasse oil (SC-SBO) was obtained at 300 bar and 333 K at the solvent flow rate of 1.2 kg/hr. The concentration of phenols and substituted phenols increased with increase in pressure. The maximum concentration of phenols (about 70%) was obtained at 300 bar and 333 K. It was also observed that the concentration of phenols in SBO obtained from unleached sugarcane bagasse was higher.

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