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Properties of Bio-Oil Produced by Co-Pyrolysis of *Calotropis procera* Stem and Waste Polystyrene

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Abstract. In this work, initially pyrolysis of C*alotropis procera* stem (CPS) was performed. Then, CPS was co-pyrolysed with waste polystyrene (WPS) taken in the proportion of 50:50 by weight of CPS and WPS. The product yields and properties of bio-oil obtained from pyrolysis of CPS and co-pyrolysis of CPS-WPS were compared. Pyrolysis experiments were carried out in a fixed bed reactor. The feedstock was heated to 500°C in inert nitrogen gas atmosphere that was allowed at a flow rate of 20 ml/min and the heating rate was maintained at 5°C/min. The pyrolysis of CPS and co-pyrolysis of CPS-WPS produced 6.28% and 47.34% bio-oil respectively. The GC-MS analysis showed that CPS bio-oil consisted of mainly phenolic compounds and few oxygenated, aliphatic and cyclic compounds. The CPS-WPS bio-oil was composed of mono-aromatics, esters and nitrogenated compounds. Bio-oil with reduced phenolic compounds and increased ester content was obtained by co-pyrolysis. The CPS-WPS bio-oil also possessed improved calorific value and viscosity.

Keywords: C*alotropis procera* stem, waste polystyrene, pyrolysis, co-pyrolysis, bio-oil.

INTRODUCTION

Biomass is considered as one of the world's biggest renewable energy source. Different kinds of biomass such as wood and their residues, agricultural and industrial wastes, perennial plants available in waste lands etc., are found to be potential sources for pyrolysis [1]. *Calotropis procera* is a wild shrub which can grow to 1-3 m height and 17–19 cm wide and it is commonly known as *Erruku* plant in Tamil. Plastics are non-biodegradable materials and it is well known that the incineration of plastics release toxic gases [3].

Co-pyrolysis is a method of using two or more feedstock in the pyrolysis reaction. The materials such as synthetic polymers (polystyrene, polypropylene, polyethylene), coal, waste tire, petroleum residue etc. can be used as co-feed in co-pyrolysis process. Many studies have identified that the process of co-pyrolysis can be used to enhance the quantity and quality of bio-oil. Polystyrene, also known as thermocol is an aromatic polymer with high molecular weight and it is used in the manufacture of several goods and as packaging material [3]. The thermal decomposition of polystyrene in the range 400-600°C mainly produces aromatic compounds such as benzene and styrene. The co-pyrolysis of biomass and polystyrene produce more polar and stable bio-oil [11]. The maximum bio-oil yield of 61.63% was obtained at 500°C in the co-pyrolysis of palm shell and polystyrene in the ratio of 50:50, whereas the palm shell pyrolysis produced only 46.13 %. [5]. The waste polystyrene when co-pyrolysed with Mahua seed in the ratio of 2:1 produced bio-oil with higher energy content, less acidity and lower viscosity [4].

In this work, pyrolysis of *Calotropis procera* stem (CPS) and co-pyrolysis of CPS with Waste PolyStyrene (WPS) were conducted to produce bio-oil. The co-pyrolytic experiments were conducted using 50:50 weight ratio of CPS and WPS and the effect on pyrolysis products yield and properties of bio-oil such as viscosity, calorific value and chemical composition were studied.

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MATERIALS AND METHODS

Fresh CPS samples were harvested from the plants grown in Puducherry, India. The collected samples were dried and milled to the size of less than 1 mm and stored. The WPS which had been used as packaging material for domestic appliances was collected, sun dried and powdered to 1 mm size and stored. CPS and WPS were blended in the ratio of 50:50 by weight and was used in the co-pyrolysis experiments.

The proximate composition, elemental composition and calorific value of CPS were determined by using muffle furnace, CHNS analyzer (make PerkinElmer, Model 2400 Series II) and bomb calorimeter (make: Rico scientific industries, model R6BT-5) respectively.

The pyrolysis experiments were carried out at a heating rate of 5ºC/min in a fixed bed reactor made up of stainless steel. The reactor was heated by an electrical heater and the reactor temperature was measured by a K- type thermocouple. The heating rate was controlled by a PID controller. The chemical compounds present in the bio-oil were detected by GC-MS (Clarus 680 GC with Elite-5MS).

Experimental Procedure for Pyrolysis and Co-Pyrolysis

Initially, 100 gm of CPS sample was pyrolysed at a heating rate of 5ºC/min to an end temperature of 500°C. Then, the co-pyrolysis experiment was carried using CPS and WPS in the weight ratio of 50:50 at the same heating rate of 5ºC/min and pyrolysis end temperature of 500ºC. The pyrolytic liquid yield, char yield and non-condensable gases yield were noted for both the cases. The collected pyrolytic liquid was noted to be aqueous in nature and hence kept in a separating funnel for one day. The bio-oil phase (top layer) and aqueous phase (bottom layer) were collected separately and weighed. The pyrolysis and co-pyrolysis experiments were repeated thrice and the average yield values were taken.

RESULTS AND DISCUSSION

Table 1 shows the proximate and elemental composition and calorific values of CPS and WPS. The volatile matter content of CPS was high and comparable with that of other ligno-cellulosic biomass like palm shell of 73.5% [12]. The WPS has 99.63% volatile matter and very less ash content. The higher oxygen content of the CPS resulted in lower energy content. Whereas, WPS due to its rich carbon content has higher energy content.

TABLE 1. Properties of CPS and WPS properties

Property	CPS	WPS [12]
Proximate composition (wt.%)		
Moisture	9.45	0.25
Volatile matter	69.15	99.63
Ash	3.80	0.0
Fixed carbon	17.50	0.12
Elemental composition (wt. %)		
Carbon	42.83	91.34
Hydrogen	6.48	7.80
Nitrogen	0.49	0.34
Sulphur	0.20	0
Oxygen (by difference)	50.00	0.52
Higher heating value (MJ/kg)	18.98	42.96

Yields of Pyrolysis and Co-Pyrolysis Products

The yields of liquid, solid and gaseous products obtained from the pyrolysis of CPS and co-pyrolysis of CPS and WPS are given in Table 2. The addition of polystyrene to biomass in the ratio 50:50 increased the total pyrolytic liquid (bio-oil phase plus aqueous phase). The total pyrolytic liquid yield increased from 42.4 % to 60.01 % of the weight of the feedstock. The bio-oil yield improved from 6.28 % to 47.34 % due to the reduction in aqueous phase content in the co-pyrolytic liquid. The reason for the increase in bio-oil yield may be due to higher volatile matter content and presence of very less moisture in WPS. Further, the char and non-condensable gas yields decreased with the addition of WPS.

TABLE 2. Yields of pyrolysis and co-pyrolysis products

Feed stock	Total liquid Yield (wt.%)	Aqueous phase (wt %)	Bio-oil yield (wt %)	Char yield (wt %)	Gas yield (wt.%)
100 % CPS	42.4	36.12	6.28	37.4	20.2
50 % CPS + 50 % WPS	60.01	12.67	47.34	26.64	13.35

Characterization of Pyrolysis and Co-Pyrolysis Bio-Oil

Fuel Properties

The calorific value and viscosity of CPS bio-oil and CPS-WPS bio-oil are shown in Fig. 1. It is seen that the calorific value and viscosity of CPS bio-oil were improved by the co-pyrolysis of CPS with WPS. The calorific value of CPS-WPS co-pyrolytic bio-oil was 18% lower than that of diesel. Its viscosity was about 3 times higher than that of diesel.

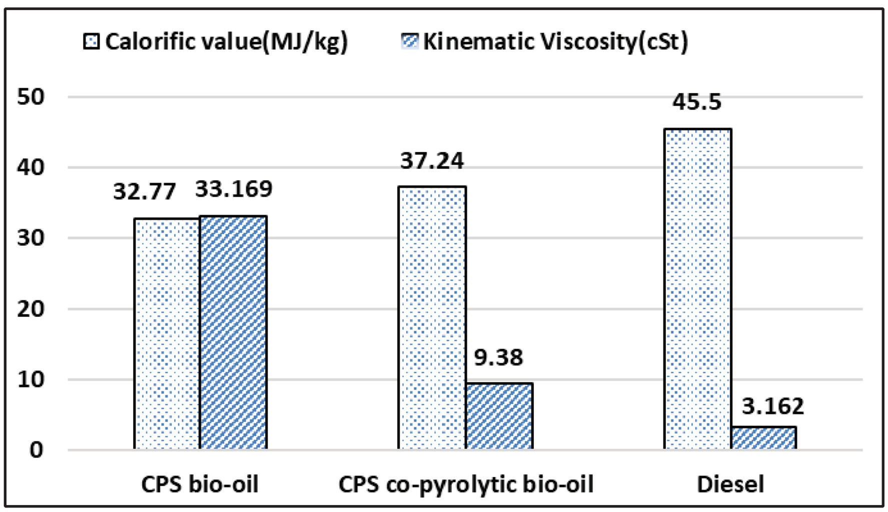

FIGURE 1. Comparison of bio-oil properties

Chemical Composition

The different chemical compounds present in the CPS pyrolytic oil and CPS-WPS co-pyrolytic oil were identified by GC–MS and are listed in Table 3. The degradation of ligno-cellulosic components by pyrolysis produced various organic compounds of different molecular structures and weights.

The compounds present in CPS bio-oil include phenols, organic acids and esters. The phenols and oxygenated compounds are around 45%. But in the CPS-WPS co-pyrolytic bio-oil, the chemical compounds present are mainly aromatics, esters and acids. The addition of WPS converted most of the phenolic compounds (decreased from 45.08 to 5.31%) into esters (increased from 5.20 to 29.43%).

TABLE 3. Chemical composition of pyrolytic and co-pyrolytic bio-oils

Chemical Compounds	CPS Pyrolytic bio-oil	CPS-WPS Co-pyrolytic bio-oil
Aromatic compounds (Furans, phenols & monoaromatics):		
3-Benzofuranmethanol, 2,3-Dihydro-2-(4-Hydroxy-3-Methoxyphenyl)-5-(3-Hydroxy-1-Propenyl)-7-Met	3.322	-
Ethanone,1-(2-Furanylcyclopropyl)-	2.715	-
1,3,4,4a.Beta.,5,6,8,9-Octahydro-4a-Hydroxy-6,6,8b-Trimethylazuleno(5,6-C)Furan-3-One	2.365	-
Phenol,2-Methoxy-4-(1-Propenyl)-, (E)-	6.092	-
Phenol,2-Methoxy-4-Propyl-	6.014	-
Phenol, 4-Ethyl-2-Methoxy-	13.323	-
Phenol, 2-Methoxy-4-Methyl-	14.545	-
Phenol, 2,3-dimethyl-	5.109	5.313
Alpha.-ethyl-o-methoxy-.alpha.-methylbenzyl alcohol	-	2.831
2-pentenol, 5-phenylo	-	5.438
Ethylbenzene	-	14.014
P-xylene	-	3.976
O-xylene	-	4.115
Styrene	-	7.140
5-oxo-6-phenylhexanoic acid	-	3.207
Aliphatic compounds:		
Hexadecane	2.216	-
9-Eicosyne	13.014	-
Nitrogenated compounds:		
3-acetyl-n-methyl-tomatidine	-	5.270
Azetidine, 3-methyl-3-phenyln	-	3.935
Oxygenated compounds (Esters and acids):		
URS-12-En-24-oic acid, 3-Oxo-, Methyl Ester, (+)-	2.866	-
Hexadecanoic Acid, Methyl Ester	2.339	-
Glutaric acid, mono-phenyl ester	-	2.215
Acetic acid, 2-phenylethyl ester	-	2.906
Acetic acid, m-tolyl ester	-	24.312
Limonene oxide, transo	-	5.716
2r-acetoxymethyl-1,3,3-trimethyl-4t-(3-methyl-2-buten-1-yl)-1t-cyclohexanol	-	4.418
N-Hexadecanoic Acid	7.710	-
Cyclic compounds:		
Ethanone, 1-(2-Methyl-1-Cyclopenten-1-Yl)-	11.573	-
2-Cyclopenten-1-One, 3,4,5-Trimethyl-	6.527	-
Tricyclo[3.2.1.0(2,4)]octane,8-methylene-, (1.alpha.,2.alpha.,4.alpha.,5.alpha.)-	-	5.438

CONCLUSION

In this study, the pyrolysis of CPS and co-pyrolysis of CPS-WPS were carried out in a fixed bed reactor at a heating rate of 5ºC/min till an end temperature of 500ºC. WPS was used in the co-pyrolysis of CPS in the weight ratio of 50:50. The yield of bio-oil from CPS pyrolysis was very low and it was found to contain mainly phenolic compounds. The co-pyrolysis of CPS and WPS improved the yield and the quality of bio-oil. The co-pyrolysis of CPS with WPS reduced the phenolic compounds and increased the ester content.

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