



Effect of catalytic vapour cracking on fuel properties and composition of castor seed pyrolytic oil



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ABSTRACT

In this work, catalytic upgrading was carried out to enhance the yield and quality of castor seed pyrolytic oil. The influence of catalytic vapour cracking of castor seed was performed over Kaolin, CaO and ZnO catalysts at various weight percentage of loading. This study confirmed that the yield varied with catalyst type and its amount of loading. The maximum pyrolysis yield of oil was obtained about 66.4 wt.%, 64.9 wt.% and 65.8 wt.% at 15 wt.% CaO and Kaolin and 10 wt.% ZnO respectively. The effect of catalyst on fuel properties were studied at that catalyst loading where the yield of pyrolytic liquid was higher. The fuel properties of castor seed thermal and catalytic pyrolytic oil were compared. The cracking of castor seed pyrolytic vapour over the bed of catalysts proved to enhance the fuel properties of pyrolytic oil for all catalysts. In comparison with ZnO, CaO and Kaolin found to have significant effect on enhancing the fuel properties in terms of viscosity, pH, calorific value and pour point. It was observed that in catalytic pyrolytic oil the number of acidic groups significantly reduced as they got converted to esters compared to thermal pyrolytic oil. The increase in the formation of nitriles and aromatics content in the catalytic pyrolytic oil was also noticed which were comparatively less in the thermal pyrolytic oil.

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1. Introduction

Crude biomass pyrolytic liquid is unstable and a mixture of organic and aqueous phase. The organic phase pyrolytic liquid is a mixture of various acids, oxygenated hydrocarbons, alkane, alkene, alcohol, ketones, furan, various aromatics, levoglucosan along with several nitrogenated compounds. Apart from these chemical compounds, water in the pyrolytic oil is a result of various pyrolysis reactions. The presence of water, various oxygenated compounds and acids reduces the stability as well as fuel quality. It is well known that the formation of water is a byproduct of biomass pyrolysis [1]. Usually, water is generated due the dehydration reaction which occurs at the initial stage of biomass pyrolysis. This also depends on the initial moisture content and the oxygen content of the feed biomass. Besides this reason, water also forms during the degradation of cellulose, hemicellulose at low temperature [1,2]. The presence of oxygen in the biomass reacts during de-volatilization of cellulose which forms various oxygenated compounds. The volatilization of cellulose increases the porosity of the biomass char particles which makes easy diffusion of oxygen into

it. Since, lignin is less reactive with oxygen, most of the oxygenated compounds produced during de-polymerization of total cellulose [2]. The oxygenated compounds include carbonyl group of compounds such as aldehyde (RCHO), ketone (RCOR'), carboxylic acid (RCOOH), ester (RCOOR'), amide (RCONR'R''), acyl halides (RCOX) and acid anhydrides ((RCO)₂O) along with the formation of gaseous products, e.g. CO, CO₂, CH₄ [3,4]. However, it is quite difficult to find the actual reaction mechanism of cellulose pyrolysis. Levoglucosan is one of such sugar compounds which are also formed by pyrolysis of cellulose. Lignin decomposition leads to the formation of phenols and aromatic compounds such as styrene, ethyle benzene and toluene due to the free-radical and ionic reaction pathways during the pyrolysis of lignin [4,5]. The primary pyrolysis of lignin results styrene, whereas the secondary decomposition of styrene produce ethyle benzene and toluene [5]. Extractives present in biomass also play a major role on the yield of organic liquid during pyrolysis of biomass. The extractive content is usually higher in the oil rich biomass such as oil containing seeds in comparison with woods, leaves, grass and other biomasses. Literature reveals that more the extractives which is a composition of various fatty acids, waxes, fats, resins, tannin, simple sugars, starches and pigment higher is yield of organic pyrolytic liquid [4,6]. Guo et al. studied the influence of extractives on the mechanism of biomass pyrolysis and observed that decomposition of extractives formed

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phenol, methanol, methane, aldehyde with fewer amounts of CO₂ and water. However, extractive free biomass resulted in less organic and acid yield and more water, CO, CO₂. It was confirmed that the presence of extractive in biomass catalyze the formation of more acids while its absence enhances the yield of water and CO₂ [4]. Hence, biomass pyrolytic oil has complex composition. Since, biomass pyrolytic oil can be used as an alternative fuel, the present research aims to produce higher and better pyrolytic oil than char and gaseous products. The yield and quality of pyrolytic oil depends on feed stock types and other process parameters such as reactor used, temperature and carrier gas flow rate. Literature says non-edible seeds are such biomass which contains high extractives compared to total cellulose and lignin. Thermal pyrolysis of various non-edible seeds and their composition was reported elsewhere, which showed the non-edible seed pyrolytic oils were acidic [7–10]. This acidic properties of the pyrolytic oil reduces its stability and also do not allow it to be used directly in combustion engine. Therefore, upgrading of the pyrolytic oil is highly desirable. Catalytic cracking and catalytic cracking of biomass pyrolytic vapours are some of the methods that can be used to enhance the fuel properties of pyrolytic oil. Pyrolysis in presence of catalyst is firmly known as catalytic pyrolysis. Catalytic pyrolysis is of two types. One is known as *in-situ* process, where catalyst is mixed with the feed biomass, whereas the other technique is *ex-situ* process. The *ex-situ* catalytic pyrolysis is known as catalytic vapour cracking, where the pyrolytic vapour generated passes through a bed of catalyst and cracking occurs. Both the catalytic processes enhance the yield and quality of pyrolytic oil. The effects of various catalysts on biomass pyrolysis were studied and their positive effects with respect to upgrading of pyrolytic oil are well documented [9–18]. *In-situ* catalytic pyrolysis of Mahua, Karanja and Niger seed were carried out by Shadangi and Mohanty using various catalysts to enhance the yield of pyrolytic oil and fuel properties [9–11]. The study confirmed that the use of catalyst enhanced the fuel properties of pyrolytic oil, whereas the yield was more or less equal with that of thermal pyrolysis process. Onay reported that the yield and quality of pyrolytic oil from *Pistacia khinjuk* seed can be enhanced using BP 3189 and Criterion-424 catalysts [13]. However, the decreased in the yield of pyrolytic oil on catalytic pyrolysis of cotton seed with MgO was reported by Putun [14]. Hence, it is confirmed that the yield and quality of pyrolytic oil varies with the catalyst types. There are many literatures found on *in-situ* and *ex-situ* catalytic pyrolysis of different biomass, however, a few were noticed on non-edible oil seeds. Based on the literatures, it was observed that catalytic vapour cracking can be used as one of the upgrading techniques to enhance the liquid yield and quality.

In the present study catalytic vapour cracking of Castor seed was studied using catalysts such as Kaolin, CaO and ZnO. The effect of catalysts on yield and fuel properties of pyrolytic oil was studied and compared with that of thermal pyrolysis reported elsewhere [8].

2. Materials and methods

2.1. Raw materials

Castor seed used as raw material in this study were purchased from Ganjam, Odisha, India. The seeds were separated from their kernel and afterwards used as the feed for pyrolysis.

2.2. Catalysts used

Three catalysts namely Kaolin (Central Drug House (P) Ltd., India), CaO and ZnO (Loba Chemie Pvt. Ltd., India) were purchased and used in the present study without any further treatment.

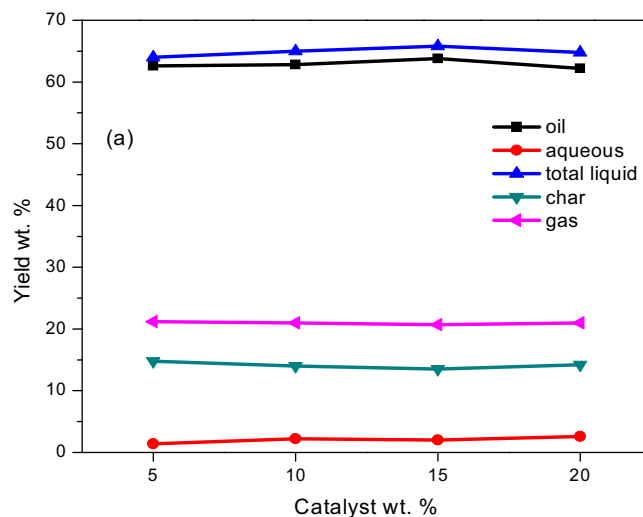


Fig. 1. Effect of Kaolin on pyrolytic yield.

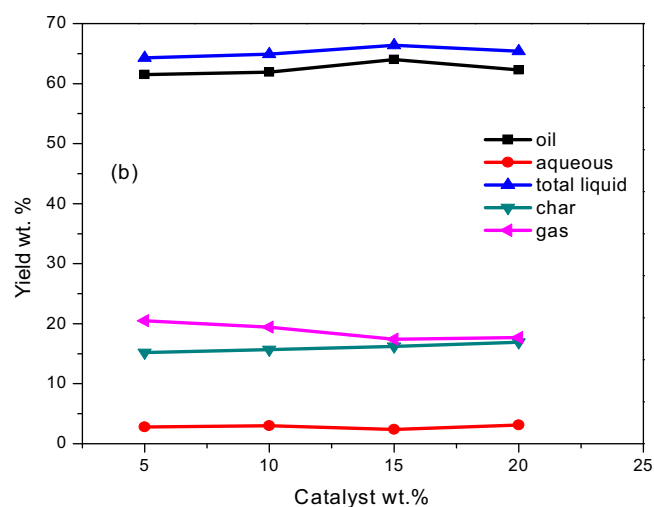


Fig. 2. Effect of CaO on pyrolytic yield.

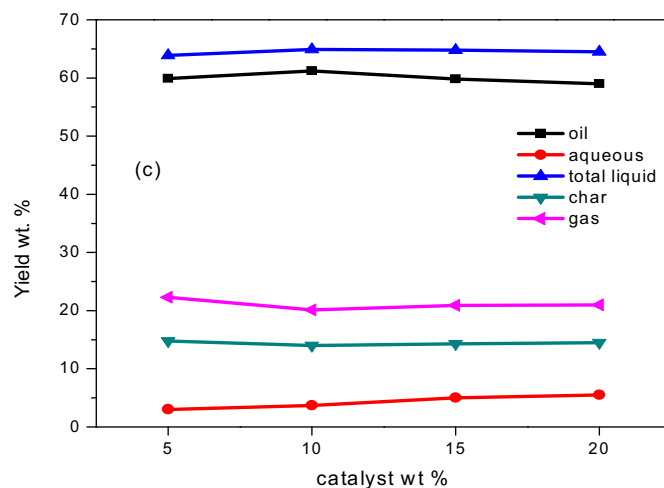


Fig. 3. Effect of ZnO on pyrolytic yield.

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