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Effect of catalyst contact on the pyrolysis of wheat straw and wheat husk

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HIGHLIGHTS

- Thermal and catalytic slow pyrolysis of wheat straw and husk has been carried out.
- Different zeolite catalysts have been screened for catalytic pyrolysis.
- Catalyst mode of contact is an important reaction parameter in pyrolysis.
- Product distribution is different in every case as decomposition mechanism varies.

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ABSTRACT

Slow pyrolysis of wheat straw and wheat husk has been carried out using microporous zeolite catalysts such as H-ZSM-5, mordenite and Y zeolite. Catalyst testing has been carried out at two positions in the reactor; one where it is mixed with the feed and other, by placing it in a catalyst boat to allow vapour phase contact. The thermal experiments have been carried out at 300, 350, 400 and 450 °C and the catalytic experiments have been carried out at 350 °C. Bio-oil yields are lower in all cases of catalytic pyrolysis of wheat straw compared to thermal run. With wheat husk, most cases of catalytic pyrolysis produced more bio-oil than thermal run. The bio-oil has been characterised using Gas Chromatography–Mass Spectrometry (GC–MS) and ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) and bio-char using Fourier Transform-Infra Red spectroscopy (FT-IR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). It has been observed that the pyrolysis product profile and decomposition mechanism is dependent on the method of contact of catalyst.

1. Introduction

The increase in the emissions of greenhouse gases worldwide along with the volatility of crude oil prices has made fossil resources a less attractive carbon source [1–3]. As on date, an important area of research in chemistry, engineering, agriculture, and environmental studies is the development of processes that utilise a sustainably produced feedstock like biomass to produce fuels/chemicals [4]. This research is of great importance to the hydrocarbon sector which is strongly dependent on petroleum, a non-renewable fossil resource. Energy can be obtained from solar, wind, tidal energy, etc. but the carbon required for liquid hydrocarbons can be obtained only from biomass in a sustainable manner. Utilisation of lignocellulosic biomass, which does not create the food vs. fuel issue, for the production of transportation fuels/chemicals is a promising alternative realisable in short time scale [5]. Lignocellulosic biomass is a natural polymer composed of cellulose, hemicellulose, lignin and few other inorganic substances. There are various methods of conversion of lignocellulosic biomass like biochemical and thermo-chemical routes. Under the umbrella of thermo-chemical routes of conversion, processes such as combustion, gasification, pyrolysis, liquefaction and carbonisation are available of which pyrolysis seems to have the highest potential for commercialisation [6]. Wheat is one of the most cultivated crops in the world especially in India and hence residues such as wheat straw and wheat husk are widely available. The biomass feedstocks are highly complex, diverse and multi-scale in nature. Pyrolysis reactions are multi-phase in nature and so this combination of multi-scale and multi-phase nature requires in-depth understanding of the reaction mechanism. There are several fundamental challenges in understanding the pyrolysis reactions such as formation of chars, breakdown into liquid products, effect of solvents and catalysts [7]. Microwave pyrolysis of wheat straw by Zhao et al. showed that pyrolysis did not occur completely even with a high microwave power of 800 W yielding around 70 wt.% residual solids. Around 50 wt.% liquid products and 22 wt.% solid

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residue was observed with 20 wt.% additives of CuO, Fe_3O_4, K_2CO_3 and Na_2CO_3 [8]. Patil et al. carried out hydrothermal liquefaction of wheat straw in water and water–alcohol mixtures and in some runs 5 wt.% Ru/H-Beta catalyst was also used. An increase in the calorific value of the bio-oil with increase in the reaction temperature was observed and catalyst was seen to promote deeper deoxygenation reactions [9]. Hydrothermal conversion of wheat husk has been carried out at 280 °C with alkali catalysts such as KOH and K_2CO_3. Total bio-oil yield and yield of light hydrocarbons (ether fraction) was found to be the maximum with K_2CO_3 solution. The heavy hydrocarbons (acetone extraction) were high with KOH (16%) [10]. Pyrolysis can be carried out in the absence (thermal decomposition) or presence of catalyst (catalytic decomposition). Sakata et al. carried out studies to understand the effect of position of catalyst for pyrolysis of plastics (polyethylene and polypropylene) and observed significant variations in the product distribution and yields [11]. In case of biomass pyrolysis, experiments on Py-GC/MS to understand the effect of position of catalyst [12–15] and some preliminary catalytic pyrolysis reports of biomass using H-ZSM-5 [16,17] are available in open literature.

The position of catalyst is a very important parameter in the pyrolysis process and in large scale it also dictates the economics of the process. The decomposition of the biomass material varies with the position of catalyst and hence, the product portfolio is different in different positions. It thus becomes highly essential to understand the structure activity relationships in every case. Hence in the present investigation, the decomposition behaviour and product profile of the thermal and catalytic pyrolysis of wheat straw and wheat husk has been studied. In addition the effect of position of catalyst for wheat straw and wheat husk has been reported for the first time.

2. Materials and methods

The wheat straw and wheat husk feedstocks have been obtained from a local agricultural farm. The catalysts used in the experiment namely mordenite (Si/Al ratio = 10:20), Y zeolite (Si/Al ratio = 5:8) and H-ZSM-5 (Si/Al ratio = 30:40) were obtained from Sud-Chemie. Surface area and pore size analysis of the catalysts used was carried out by physisorption of N_2 at 77 K using ASAP-2010 instrument of Micromeritics (USA). The feed and reaction products were physico-chemically characterised using analytical methods described in our previous work [18].

Thermal pyrolysis of wheat straw and wheat husk were carried out at various temperatures of 300, 350, 400 and 450 °C and catalytic experiments were carried out at 350 °C under atmospheric pressure of nitrogen. The batch fixed bed reactor is made up of SS316 (length: 400 mm; i.d. 25 mm) and K-type thermocouples have been used as shown in Fig. 1. The feed samples used in this study were milled in a laboratory ultra-centrifugal mill mounted with a 1-mm screen. The sample then obtained was sieved in standard mesh to obtain particle size of 0.5–1 mm. At first, 10 g of the feed (wheat straw or wheat husk) was loaded into the reactor and in case of catalytic reactions; 1 g of catalyst was either mixed with feed (solid phase contact (SPC)) or kept in the catalyst boat (vapour phase contact (VPC)) as shown in Fig. 2. The reactor was purged with nitrogen to remove the inside air and nitrogen flow rate during pyrolysis was 50 ml min^{-1}. The starting temperature was the ambient room temperature at 25 °C and the heating rate to reach the pyrolysis temperature was set around 25 °C min^{-1}. Once final pyrolysis temperature was attained, the reactor was maintained at the required temperature for a period of 1 h to ensure that all condensable vapours were collected. Biomass bed temperature has been taken as the pyrolysis temperature and another thermocouple indicated the skin temperature of the reactor. The vapours

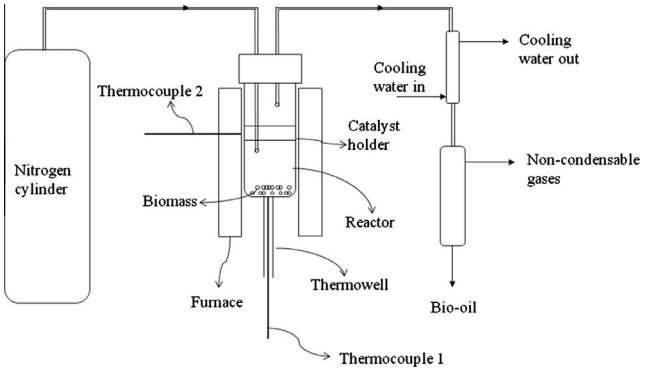

Fig. 1. Experimental unit.

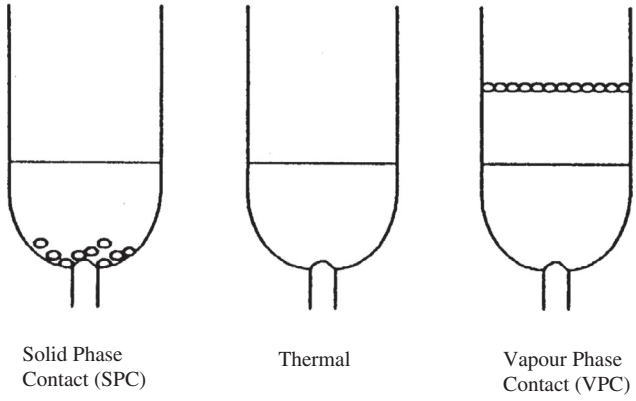

Fig. 2. Method of contact of catalyst inside reactor.

formed after the reaction was condensed using cooling water maintained at 2 °C. The liquid products were collected after a cooling period 1.5–2 h. Water in bio-oil was removed by the addition of sodium sulphate and acetone was used to recover the organic fraction. Conversion as defined in this process is the amount of solid that has been converted into liquid or gaseous products. The remaining solid after the reaction left in the reactor is termed as bio-char. The experiments have been carried out in duplicates/triplicates and the average values with a standard deviation within ±1.0% have been reported. The solid bio-char has been characterised after manually separating the catalyst in case of solid phase contact.

Bio-char yield, wt.% = (Weight of reactor after reaction) − (Weight of empty reactor)
Gas yield, wt.% = 100 − (Bio-oil yield, wt.% + Bio-char yield, wt.%)
Conversion, % = 100 − (Bio-char yield, wt.%)

3. Results and discussions

The ultimate analysis of wheat straw was found to be carbon (41.19 wt.%), hydrogen (5.34 wt.%), nitrogen (1.4 wt.%) and sulphur (0.096 wt.%). In case of wheat husk, the ultimate analysis was as follows: carbon (38.53 wt.%), hydrogen (5.24 wt.%), nitrogen (1 wt.%) and sulphur (0.381 wt.%). The gross calorific value of wheat straw and wheat husk was found to be 17.2 and 15.33 MJ kg^{-1} respectively. Moisture and ash content of wheat straw was 6.6 and 8.19 wt.% respectively and that of wheat husk was 7.73 and 13.91 wt.% respectively. The composition analysis showed that both the feedstocks majorly were composed of holocellulose (wheat straw – 70.76% and wheat husk – 59.09%). The