Effect of temperature and pressure on the hydropyrolysis of cotton residue

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Abstract

With growing concerns of fossil fuel resources availability and the volatility of crude oil price, it is becoming imperative day by day to utilize the renewable sources of energy in a sustainable, environment friendly and energy efficient manner. India is the world's second largest producer of cotton after China. Cotton residue is one of the most abundant agricultural residues after rice and wheat residues but has the characteristics of forest residues. The hydropyrolysis of cotton residues has been carried out at various pressures (1, 20 and 40 bar) and temperatures (300-450°C). The effect of temperature and pressure have been studied to understand their yield patterns and it has been observed that 20bar pressure and 400°C are the optimum conditions. The TG analysis shows that cotton residue has two significant decomposition temperatures. The SEM, XRD patterns and FT-IR spectra clearly indicate the decomposition of the macromolecular structure of the cotton residue as the functionalities present in the feed are lost after hydropyrolysis.

Keywords: *cotton stalks, cotton ginning waste, hydropyrolysis, bio-oil, bio-char*

1. Introduction

As on date, an important current focus of research in chemistry, engineering, agriculture, and environmental policy is the development of clean technologies that utilize a sustainably produced feedstock like biomass to the largest extent possible [1]. This research is especially important in the hydrocarbon sector which is strongly dependent on petroleum, a non-renewable fossil source of carbon. However as the world wide supply of petroleum diminishes, it is becoming increasingly expensive and, accordingly, less attractive as a carbon source. Second generation bio-fuels are obtained from non-edible sources such as agricultural and forest residues etc. unlike the first generation bio-fuels which are made from edible sources of biomass. Cotton is produced in huge quantities all over the world and this is accompanied by generation of tons of cotton waste each year. Cotton plant waste refers to the residue left unused in the field after cotton is harvested. Cotton gin waste typically includes products from the ginning process not including seed or lint [2]. Burning of cotton stalks should be avoided as nutrients are lost and soil carbon levels decline quickly but this is the most followed process as on date all over the world [3]. Cotton residue, a lignocellulosic biomass, is made up of cellulose, hemicellulose, lignin and other inorganic matter.

Owing to the availability and its non-competence as food or fodder, cotton residue can be a suitable feedstock for renewable hydrocarbon production. It is observed that the cotton residue has the characteristics of forest residue although it is an agricultural residue [4]. Researchers all around the world have subjected cotton residue to various processes of conversion and several products have been obtained yet there are no reports of hydropyrolysis of cotton residue in the open literature.

There are several methods of conversion of biomass which can be grouped as bio-chemical, chemical and thermo-chemical methods of conversion. The thermo-chemical methods of conversion do not require the energy intensive pre-treatment step as in the bio-chemical methods and hence, it can utilize the feedstock as such. Due to the disadvantages of fast pyrolysis bio-oil such as high TAN, high oxygen content and poor miscibility with crude oil and their distilled fractions, process of hydropyrolysis has been used to produce value added hydrocarbons [5]. In this process, hydrogen at high pressures is used and pyrolysis occurs at high temperatures of 350-450°C.

In this paper, we have carried out the hydropyrolysis of cotton residue and the optimal conditions for the same have been evaluated. The products of hydropyrolysis have been characterized and evidences for the opening of the macromolecular structure have been provided.

2. Materials and Methods

The feedstock cotton residue has been obtained from an agricultural farm in Andhra Pradesh, India. The thermo-gravimetric analysis, trace metal analysis, SEM, XRD and FT-IR of cotton residue has been carried out. In addtition, the mositure content and calorific value have also been found out.

The designed prototype hydropyrolysis reactor is heated electrically which is controlled by a temperature programmed controller. The thermocouples are placed in the skin and in the heart of the reactor inside the thermowell provided. The gas from the hydrogen cylinder

is passed into the reactor and the needle valve controls the pressure in the unit. The product stream from the reactor is sent into a condenser. The non condensable gases are collected in a tedler bag for gas analysis and liquid is collected separately.

The hydropyrolysis of cotton residue has been carried out at various temperatures of 300, 350, 400 and 450°C and pressures of 1, 20 and 40 bar with a heating rate of 30°C/min. The oven dried feedstock is weighed (20 g) and loaded into the reactor. The reactor is then placed in the furnace and pressurized using hydrogen gas till the desired value of pressure is reached and then the flow is stopped. The required final temperature and heating rate are set and the final temperature is maintained for 1 h or until the gases evolve whichever is earliest. The pressure is maintained constant by intermittently removing the products from the system. The products are finally collected separately and analyzed on a carbon paper coated adhesive followed by gold coating.

3. Results and Discussion

The TG/DTG of cotton residue showed two significant decompositon temperatures. Na, Mg, P and Ca are major elements present in the feedstock naturally occurring in their structure. The gross calorific value of the feed has been found out as 16.08 MJ/kg.

It can be seen from table 1 that with increase in temperature from 300 - 400°C, there is an increase in the yield of bio-oil. At 450°C, the yield of bio-oil is seen to be decreased due to secondary reactions. It can also be observed that the yield of gases has increased which is attributed to high temperatures and cracking of high molecular weight hydrocarbons to low molecular weight non-condensable hydrocarbons with 2°C cooling water.

With respect to pressure, it can be observed that the yield of bio-oil increases from 1 bar to 20 bar and drops when pressure is increased to 40 bar. At higher temperatures of 350 - 450°C, it can be observed that with increase in pressure from 20 bar to 40 bar, the yield of bio-char is increased. This is in line with the results of open literature that presence of vapours in the vicinity of char leads to increased production of char. This is a combined effect of increase in temperature and pressure.

The bio-char produced by hydropyrolysis of cotton residue has been characterized using SEM, XRD and FT-IR. It has been observed that the macromolecular structure of the cotton residue has been decomposed. The significant functionalities present in the cotton residue do not exist after hydropyrolysis. The porous nature of the cotton residue bio-char is clearly evident at 400°C and 20 bar beyond which the structure seems to have collapsed.

Table 1. Hydropyrolysis of cotton residue yields

Pressure, bar	Bio-oil, wt.%	Gas, wt.%	Char, wt.%	Conversion, %
300°C				
1	6.8	38	55.2	44.8
20	8.2	35.7	56.1	43.9
40	5.8	38.2	56	44
350°C				
1	12.6	46.5	40.9	59.1
20	14.5	40.5	45	55
40	12	39	49	51
400°C				
1	15.1	44.7	40.2	59.8
20	18.7	38.7	42.6	57.4
40	13.2	42.3	44.5	55.5
450°C				
1	14.9	47.8	37.3	62.7
20	18.3	43.7	38	62
40	13.1	46	40.9	59.1

4. Conclusions

Cotton residue is an interesting feedstock for thermo-chemical methods of conversion to produce value added hydrocarbons in a sustainable manner. Hydropyrolysis of cotton residue has been carried out and it has been observed that the optimum conditions in the used experimental set up at 400°C and 20 bar pressure of hydrogen. The data obtained by the analytical techniques have provided supplementary information to arrive at this result. When hydropyrolysis is integrated with hydroconversion, fungible hydrocarbons can be obtained directly from this process.

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