International Journal of Emerging Trends in Engineering and Basic Sciences (IJEEBS)
ISSN (Online) 2349-6967
Volume 9, Issue 2 (March-April 2022), PP.08-11

Decomposition of Agriculture Biomass waste by Pyrolysis

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Abstract :- Agriculture waste biomass is the sustainable resource for renewable energy. This biomass can be converted in the valuable product by thermo-chemical conversion. Pyrolysis is the technique that converts the biomass residue into the valuable products by thermo-chemical decomposition. This paper reviews the physicochemical properties of biomass, pyrolysis process and discusses the distribution of pyrolysis product (Char, Bio-oil and Gases) based on the physicochemical properties, heating rate and temperature. Furthermore the review was summarized to improve the bio-oil yield.

Keywords: Pyrolysis, Agriculture biomass waste, Fast pyrolysis, thermo-chemical decomposition

1. Introduction

The consumption of fossil fuel like Coal, Petroleum and Natural gas has been increased due to increasing population. In order to meet the energy related needs of the growing population, it has become necessary to develop new energy sectors. In rural area huge amount of agriculture biomass waste generated that can be use as renewable energy sources. After harvesting the valuable product/part of crop, the remaining parts of the crop is left on the crop field as a solid waste/residue is called agriculture biomass waste (Venkatramanan et al.,2021). In India, major crop that are contributed to generate the solid residues on crop field are the rice, wheat, coarse cereals, pulses, oilseeds, sugarcane, cotton, jute and Mesta (Dennis Cardoen et al. 2007). The coarse cereal crops mostly include maize, sorghum, ragi, bajra, small millets and barley and pulse crops include red gram, black gram, green gram, gram, lentil and other pulses. The crops include groundnut, rapeseed and mustard, sesamum, linseed, castor seed, niger seed, safflower, sunflower and soybean are the oilseed crops. Due to agricultural extent, intensification of agriculture and farm mechanization the crop residue generation is increases day to day. In the year 2017–18 it was 516 million tonnes. (Venkatramanan et al.,2021). Major constituents of biomass waste are carbon (48.0-50.4%), oxygen (42.5-44.9%) and hydrogen (6-6.2%). Some amount of Nitrogen (0.68-0.86%), sulfur (0.21-0.25%) and ash (7.9-9.9%) is also present (Serio et al.2001).

Mostly, the crop generated biomass is burn in the crop field, during burning pollutant species releases its included CO_2, CH_4, NOx and N_2O emission of these gases is the main cause for green house effect and global warming. Venkatramanan et al.(2021) reported that, the total biomass burned between 1950 to 2018 increased from 18 million tons to 116 million tons.

Pyrolysis is the technique that converts the biomass residue into the valuable products (char, bio oil and gases) by thermo-chemical decomposition in absence of oxygen (Sundaram et al.,2009). Temperature range for this process is 250 to 900 ºC (Agata et al., 2021). Pyrolysis process is classified based on the heating rate slow and fast.

2. Pyrolysis Process

In the pyrolysis process solid biomass is heated in tubular reactor in absence of oxygen. This reactor was also classified based on the bed characteristics fixed bed and fluidized bed. Tubular reactor is the cylindrical reactor in which the biomass is placed. Whole assembly is externally heated by some external heat source or electrical heater/electrical furnace. Thermocouples were used to measure the furnace temperature, pyrolysis reactor temperature, and outlet temperatures. Pressure gauges and flow measuring devices is also provided to measure the reactor pressure and flow of carrier and outlet gases. The condensable vapours coming out with gases product is condense by using condenser. Below the condenser catch pot is used to collect the bio liquid/bio-oil. In this process Nitrogen gas is used as a inert/carrier gas.

Sundaram et al.(2009) studied the Pyrolysis of coconut shell in stainless steel tubular reactors of 200 and 300 mm length *m* and an internal and external diameter of 27 *mm* and 33 *mm* respectively. This reactor was placed inside the electric furnace with the capacity of 2 kWh for heating.

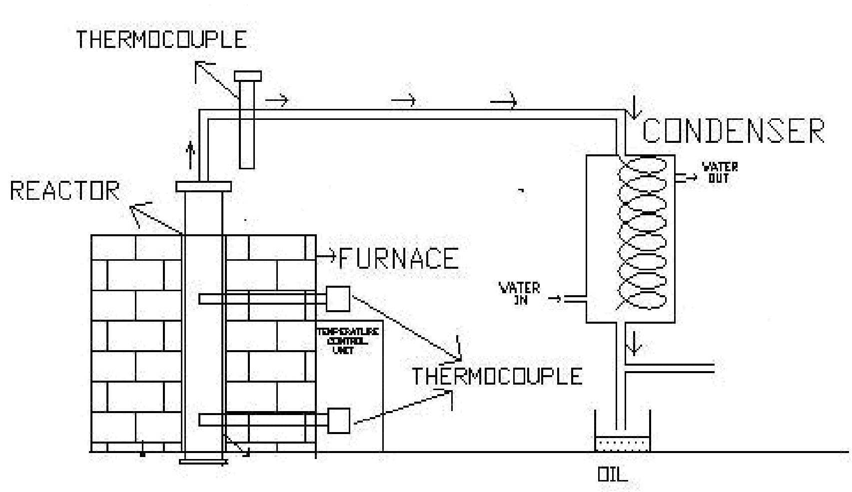

Figure1: Pyrolyser (Sundaram et al.2009)

Asadullah et al.(2008) has carried out pyrolysis of Jute stick in a reactor made of stainless steel with the height of 66 cm. The fluidized bed section of 7 cm height and 3 cm internal dia is located just at the middle of the reactor. The internal diameter of the upper part of the reactor just after the fluidized bed section is larger (5 cm) so as to decrease the gas turbulence.

In pyrolysis of biomass thermal degradation takes placed at 250 ºC temperature. Volatile matters from biomass start to vaporized. Gases generated during pyrolysis process mostly contain condensable vapour and non condensable gases. Condensable vapours get condensed in a condenser as collected as bio-oil. Valuable non condensable gases get compressed and stored. Residue remain in the reactor is a carbon rich solid called as char. The yields of the pyrolysis products solid liquid and gas depend on the biomass composition, especially its hydrogen-to-carbon (H/C) ratio, and process parameters such as the heating rate, pressure, temperature, and residence time (Agata et al., 2021). Heating rate affects the pyrolysis behaviour and product distribution of the pyrolysis products (Haykiri-Acma et al., 2006).

3. Slow Pyrolysis:

Slow pyrlysis is a process in which heating rate is less than 50 ºC/min. residence of material in the reactor is large. Sundaram et al. (2009) conducted the experiment to determining the optimum process conditions to maximize the liquid yield from the slow pyrolysis of coconut shell in a fixed bed reactor. The maximum liquid yield of 45 wt% was obtained at 550 ºC temperature with heating rate of 60 ºC/min. The heating value of the obtained bio-oil is found to be similar to that of diesel fuel. The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose and phenolic and methoxy groups produced by pyrolysis of the lignin.

Experiment conducted by Ozlem, and Kockar, (2004). Also shown that after increasing temperature bio oil yield is increases upto 550 ºC temperature and then decreases. Reported Maximum bio-oil yield at 550 ºC is 46.7%. also observed that the bio-oil yield was increases by use and increase the rate of sweep gas (Nitrogen). Chouhan .(2015). Studied Pyrolysis of cotton stalk at 600 ºC temperature with 20 ºC/min. heating rate. Result indicated that, 17.14 % bio-oil, 38 % charcoal and 44.86 % pyro gases was produced. Less bio-oil produced by this method indicated that Na and K contents are increased the charcoal and pyro-gases.Pressurized Pyrolysis of Wheat Straw Using a Tubular Reactor at 500 ºC results shows that, increases in pyrolytic pressure the gases yield decreases with increasing bio-oil yield. Result also shows that the The gas analysis at different pressures showed that 20 psi was the optimum pressure for producing syngas. At 20 psi, the CO and H2 content were high, with almost no percentage of CO2. The yield of gas was also high at 20 psi compared to 30 and 40 psi (Mahinpey et al., 2009) In the recent study, pyrolysis of oat straw carried out by Agata et al., (2021) under nitrogen atmosphere in the temperature range of 300-600 ºC, author concluded that a higher process temperature leads to an increase in the gas and liquid yields. Also confirm that, the reduction in the O/C ratio enhances the properties of the chars, gas product contain maximum CO and CO2 and H2 contain was increases with increasing temperature.

Table 1: Elemental Analysis of Biomass, Operating parameters and Product yield of Slow Pyrolysis.

Sr. N.	Agriculture Waste	C%	H%	O%	H/C	O/C	Heating rate	Pyrolysis Temp.	Swept gas	Charcoal	Bio-oil	Gas	References
1	Coconut shell	53.73	6.15	38.45	1.37	0.54	60 °C/min	400°C to 600°C .	nitrogen flow	32 to 22 wt%.	38 to 43 wt%	30 to 33 wt%	(Sundaram et al. 2009.)
2.	Rapeseed	62.1	9.1	24.9	1.75	0.3	60 °C/min ,	400°C to 700°C .	nitrogen flow 100 cm³/min	24.5% to 18.3%	(41.4% to 44.5% 46.7% at 550°C without nitrogen flow) 51.7% with N2 flow 100 cm³/min	34.1 to 37.2	(Ozlem, and Kockar, 2004)
3.	Cotton stalk (Gossypium arboretum)	41.21	4.92	51.89	1.43	0.9	20 °C/min	600 °C	nitrogen flow 20 ml/min	38%	17.12%	44.8 %	Chouhan 2015.
4.	Oat Straw	43.97	6.16	48.95	1.68	0.83	-----	300°C 600°C	50 ml/min	48% 24.0%	--- 56.9%	--- 19%	(Agata et al., 2021)
5.	bagasse	47.3	6.2	46.2	1.57	0.73	20°C/min	850°C	---	10.0%	---	---	(Rolando et al.,1995)
6.	Wheat straw	40.78	5.840	52.919	1.72	0.97	12 °C/min	500°C	50 cm3/min	char at 40 psi 32%	37.6%	30.4%	(Mahinpey et al., 2009)
7.	rice husk corn stalk	48.78 47.09	6.59 6.17	40.90 37.55	1.62 1.57	0.63 0.59	rice husk corn stalk	350 °C 600 °C 350 °C 600 °C	---	46 wt.% 31 wt.% 38 wt.% 27 wt.%	44% 46% 47% 47%	10 wt.% 23 wt.% 15 wt.% 26 wt.%	
8.	jute stick	49.79	6.02	41.37	1.45	0.62	50 °C/min	500 °C	200 mL/min	22.60 wt%	66.70 wt%	10.70 wt%	(Asadullah et al.,2008)
9.	Gromdnut shell SKT RKO	34.63 37.36		51.93 49.11		0.81 0.98	50 °C/min	---	---	32.96 at 500 °C 29.51 at 600 °C 29.20 at 650 °C	33.26 at 500 °C 37.21 at 600 °C 27.69 at 650°C	32.43 33.28 43.11	(Mohammed et al. 2016)

4. Fast Pyrolysis

Experiment conducted by Ozlem, and Kockar, (2004) to study the effect of fast pyrolysis of rapeseed with a heating rate of 300C/ min. fast heating breaks heat and mass transfer limitations and the bio-oil yield reach a maximum. Reportedbio-oil yield was 68% at 550 ºC temperature.

Salehi et al.(2009) studied the fast-pyrolysis of Sawdust at different parameters like pyrolysis temperature, heating rate, and nitrogen gas flow rate results showed that these parameter had significant effects on the yields of the oils, char, and gas. Observed that bio oil yield was decreases with increasing nitrogen flow due to short residence time in the condenser. Also confirm that the oil yield is increases with increasing heating rate because of breaking of the heat- and mass transfer limitations by high heating rates. Also confirmed that the char yield was decreases with increasing temperature and oil yield was increases upto 500 ºC than decreases.

In the Rapid pyrolysis of bagasse performed by Rolando et al.(1995) The effect of heating rate, temperature, particle size on the product distribution, gas composition and char reactivity have been studied. Shows that rapid heating rate produce less char and chars produced by rapid pyrolysis are more reactive in gasification than those produced by slow pyrolysis this is due to quick devolatilization of biomass in rapid pyrolysis results in formation of char with high porosity and high reactivity. Also studied that the char yield decreases when temperature is increased from 800°C to 1000°C and gases yield is increases. the major constituent of gas mixture is CO, H2 and CO2 (The composition of gases mixture at800°C is H2 37.5%, CO 37.9% and CO2 12.8% and at 1000 ºC H2 34.1%, CO 46.4% and CO_2 7.4%) this results shows that at high temperature CO2 concentration is reduces.

Table 2: Elemental Analysis of biomass, operating parameters and product yield of Fast Pyrolysis.

Sr. N.	Agriculture Waste	C	H	O	H/C	O/C	Heating rate	Pyrolysis Temp.	Swept gas	Charcoal	bio-oil	gas	References
1.	Rapeseed	62.1	9.1	24.9	1.37	0.54	300°C /min	400°C to 600°C.	nitrogen flow 100 cm³/min	---	68% at 550°C	---	(Ozlem, and Kockar, 2004)
2.	Sawdust	49.30	6.39	44.19	1.75	0.3	1000 °C /min	500 °C	2 LPM	17.6%	44.4%	Appx 38%	(Salehi et al., 2009)
3.	bagasse	47.3	6.2	46.2	1.43	0.9	Fast pyrol.	1000 °C	---	5.5	0.3	81.2	(Rolando et al.,1995)

5. Conclusion:

To fulfil the energy need of increasing population it has become necessary to identify the alternative of fossil fuel. Agriculture biomass waste is may be the sustainable alternative source of fuel. Paralysis is one of the technologies that may used to convert biomass into valuable energy product like Char, Bio-oil and Gases by thermo chemical conversion. In this paper review is focus to enhance the bio-oil yield. Critical literature review shows that yield of bio-oil depend on the heating rate, swept gas flow rate, pyrolysis temperature and O/C ration in biomass. Table 1 and 2 shows that fast heating of biomass increase the bio-oil yield because of breaking of the heat- and mass transfer limitations by high heating rate. Flow rate of swept gas is affect the bio-oil yield, very high flow rate reduce the residence tie of the condensable gases and reduces the bio-oil yield. Higher pyrolysis temperature reduces the bio-oil yield and lower pyrolysis temperature increases the char yield. O/C ratio is also playing an important role in pyrolysis process. Higher O/C ratio in biomass increases the gases yield and reduces the bio-oil yield.

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