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A system level analysis of pyrolysis of cotton stalk biomass

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Abstract

In this study, a system level analysis of pyrolysis of cotton stalk biomass is carried out in ASPEN Plus software to analyze the conversion of such agriculture residue into bio-oil, biochar, and non-condensable gases. The liquid and solid components are considered as primary products, whereas gases are combusted in the presence of air to generate flue gases. The flue gases are utilized to provide heat energy for reaction and drying operations. The process plant scale model is found suitable to auto-thermally process 10 tonnes/day of any biomass feed and can be extended with comprehensive kinetics for analyzing the rate of formation of value-added chemical compounds, which can be separated and used for commercial applications.

Keywords: Pyrolysis; Biomass; Cotton Stalk; Bio-oil; Biochar; Modelling.

1. Introduction

In the 21st century, the world is still relying on fossil fuel, but as per the increasing population and demands, nonrenewable sources will not be able to sustain for long. To solve the sustainability problem, world is looking for new, renewable, and clean sources of energy. The thermochemical conversion of solid biomass to energy has gained a lot of attention as it is also solving the problem of solid waste management along with being a sustainable energy source. These thermochemical processes include Combustion, Pyrolysis, Gasification, and Hydrothermal Liquefaction [1]. Among these thermochemical processes, pyrolysis is the preferred technique because of its ability to locally convert biomass into valuable products.

Pyrolysis is the technique in which low-density biomass is thermochemically decomposed at high temperatures in the absence of oxygen to convert the biomass into high-density bio-oil, biochar, and non-condensable gases (NCG). These products can be further treated and used in the other application areas like bio-oil can be used as a transportation fuel, biochar can be used as an adsorbent and NCG can further be converted to flue gases which can be used to provide energy to the reactor [1]. Agriculture residues like wheat straw, cotton stalk, rice husk, jute fibers, etc. have created a lot of concerns in India because of the mismanagement and open burning of the waste products causing pollution problems, mainly in northern states of India [2]. All these agricultural residues can be treated and converted to a valuable product using pyrolysis or other thermochemical decomposition [3,4,5]. In this study pyrolysis of the cotton stalk has been taken for the conversion from biomass waste to a valuable product.

A vast literature can be obtained on the pyrolysis of cotton stalk but majorly on lab-scale feed of biomass. Pütün [6] and Pütün et al. [7] studied the product quantity and quality of cotton stalk when the biomass was pyrolyzed at different temperatures, particle size, and nitrogen gas flow rate. The batch process was carried out in a 40 cm^3 tubular reactor and 400 cm^3 fixed bed reactor with a limited feed supply of cotton stalk biomass. Fu et al. [8] studied the characteristics and compounds present in the NCG and biochar being produced by the pyrolysis of the cotton stock. They worked on the lab scale quartz tubule reactor with the batch feed load of 10 mg. Further Chen et. al. [9] studied

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the pyrolytic polygeneration process using pyrolysis of cotton stock in a packed bed reactor. The major finding of their study was to investigate the structure of the solid, liquid, and gas products of the pyrolysis process. They carried out their study in a 620 cm^3 packed bed reactor with a 3 g biomass feed. In pyrolysis, some researchers have included torrefaction as an important method to increase the quality of the pyrolyzed product. Chen et. al. [10] studied the effect on product yield and its quality when cotton stalk biomass was firstly torrefied at different temperatures and then fed to the pyrolizer. The study of pyrolysis of the cotton stalk was further extended by Xie et. al. [11] with the use of a solar simulator to provide the heat in the pyrolizer. They used the molten salts mixture of Lithium, sodium, and potassium carbonates to increase the gas yield of 1 gm biomass in a lab-scale study. In the practical world, waste is not limited to a single component and to study that, experiments were done on the co-pyrolysis of the waste tire and cotton stalk by Shah et. al. [12]. They varied the blend ratio of both the feeds and captured the variation in the bio-oil product quality and quantity. A study on cotton stalk was also extended by Afif et. al. [13] when they carried out the lab-scale pyrolysis of the cotton stalk to estimate the quality of the solid product being produced during the process.

Since the pyrolysis process involves significant number of components in the product, the modeling of the process is on complex side. Xianjun et al. [14] developed a yield-based model for the pyrolysis of rice stalk biomass to study the effect of reactor temperature on the yield of coke and bio-oil leaving the scope of plant scale modeling studies for the process. Fedyukhin et al. [15] developed a gasification model to estimate the optimum conditions for running the process. The study involved all the primary plant operations; however, energy integration has not been carried out. Along with the yield -based studies, few kinetic-based models have been developed [16, 17, 18, 19, 20] for the pyrolysis process involving 10 to 150 reactions in the model. The above-mentioned models are concentrating on either the reactor conditions or the parametric and sensitivity analysis of the process. Plant scale modeling has been conducted by Sharma et al. [21] and their model has combusted gases and part of biochar product to supply heat energy to the plant.

To the best of the author's knowledge, majorly the literature includes lab-scale studies on the pyrolysis of cotton stalk. In case of process modeling, limited studies have been found on the system level analysis. In this article, a plant scale model of cotton stalk pyrolysis has been proposed on a commercial feed basis of 10 tonnes/day. The model starts with pre-processing of cotton stalk using grinders, separators, and driers to further converting the biomass into different products and finally separating those products for further use.

Table 1. Properties of cotton stalk feed.

Proximate Analysis (wt.%)		Ultimate Analysis (wt.%)	
Moisture	40	Carbon	51.40
Volatile Matter	75.22	Hydrogen	4.00
Fixed Carbon	21.46	Nitrogen	1.33
Ash	3.32	Oxygen	43.24
		Sulphur	0.03

2. Process description

To study the modelling of the pyrolysis of cotton stalk, biomass feed properties have been taken from Chen et.al. [9]. The proximate and ultimate analysis of biomass feed are shown in Table 1. The modelling of pyrolysis of the cotton stalk has been studied on ASPEN Plus software using a package of Redlich-Kwong-Soave cubic equation of state with Boston-Mathias alpha function (RKS-BM) for all thermodynamic properties. The model has been developed using the following assumptions.

- Reactor hydrodynamics are not considered.
- Heat losses are ignored.
- Pneumatic conveying of biomass has not been modelled.
- Process utilities are assumed to enter the plant at 25°C and 1 atm.

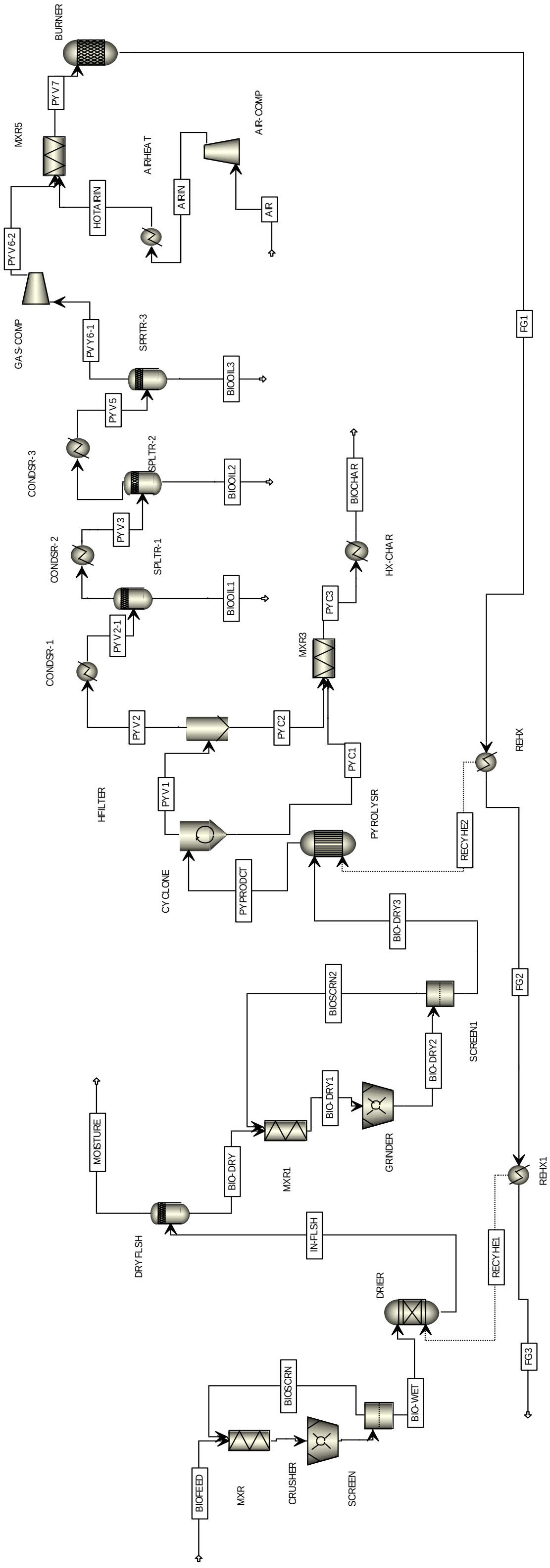


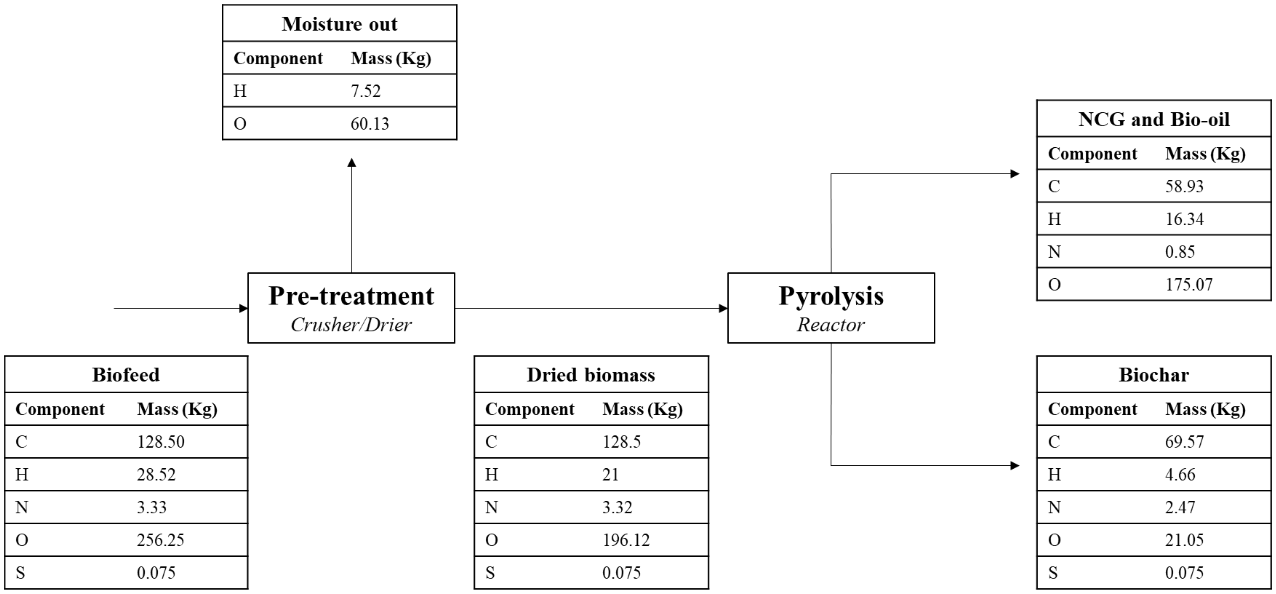
Fig. 1. Aspen Plus model of pyrolysis of cotton stalk

- Storage units are not modelled.
- Bio-oil component yield of 96.1% taken from Chen et.al. [9] has been extrapolated to 100%.
- Biochar ultimate analysis has been estimated by balancing the atoms (C/H/N/O/S) across the plant.

The ASPEN Plus model for the study as shown in Fig. 1 has been developed with the help of literature [21]. In pre-processing of biomass, 10 tonnes/day of feed is grinded and screened to a maximum particle diameter of 2 mm. The initial moisture content of 40% is then decreased using a rotary dryer which operates at $105\ °C$.

After pre-processing, the feed goes to a pyrolysis reactor which works at $550°C$. In ASPEN Plus software, a yield-based reactor RYield has been used as a pyrolysis reactor with a product yield of 32% NCG, 40% bio-oil, and 28% biochar taken from Chen et.al. [9].

The product stream of the pyrolysis reactor contains solid and gas phase products which are separated using a cyclone separator. The gaseous stream of the separator is then fed to the hot gas filter for the removal of the remaining solid product. The final solid streams coming out of the cyclone separator and filter are firstly mixed and then cooled to atmospheric temperature and stored as biochar. This biochar can further be used as an adsorbent, soil conditioner, construction material, etc. The gas stream of the filter is then cooled and flashed at different temperatures to condense volatiles from the stream. These condensed volatiles are collected as a bio-oil product which can be further modified and used as a transportation fuel. Finally, NCG is compressed and burned in the presence of air to convert the NCG into the flue gas. This flue gas contains a high amount of energy which is extracted and supplied to the pyrolysis reactor and the drier.



Moisture out

Component	Mass (Kg)
H	7.52
O	60.13

NCG and Bio-oil

Component	Mass (Kg)
C	58.93
H	16.34
N	0.85
O	175.07

Biofeed

Component	Mass (Kg)
C	128.50
H	28.52
N	3.33
O	256.25
S	0.075

Dried biomass

Component	Mass (Kg)
C	128.5
H	21
N	3.32
O	196.12
S	0.075

Biochar

Component	Mass (Kg)
C	69.57
H	4.66
N	2.47
O	21.05
S	0.075

Fig. 2. Atom balance across the reactor

3. Results and Discussion

The pyrolysis of 10 tonnes/day of cotton stalk biomass generated 2.35 tonnes/day of biochar and 3.35 tonnes/day of bio-oil after removing moisture from the feed.

3.1. Feed pre-processing

In the plant, firstly, biomass is pre-processed using grinders, drier, and screens. The first grinder crushes the biomass to a maximum particle diameter of 10 mm and then passed to a screen. The oversized particles are returned to the grinder and filtered biomass particles are moved to the rotary dryer. The dryer operates at 105 °C to decreases the moisture content of biomass from 40% to 28% while consuming 67 kW of energy. After removing 1.62 tonnes/day of water using flash vaporization, the biomass is grinded again and screened to a maximum diameter of 2mm.

Table 2. Bio-oil and NCG yield

Bio-oil		Non-Condensable Gases (NCG)	
Components	Yield (wt.%)	Components	Yield (wt.%)
Formic Acid	3.53	Carbon monoxide	27
Acetic Acid	34.49	Carbon dioxide	67
2-Propanone,1-hydroxy-	6.35	Hydrogen	1
Acetic acid, hydroxy-, methyl ester	1.37	Methane	5
1-Hydroxy-2-butanone	2.81		
Furfural	3.26		
Pyridine,2-methyl-	0.69		
2-Furanmethanol	3.95		
2-Propanone,1-(acetyloxy)-	1.65		
2(5H)-Furanone	2.33		
2-Cyclopenten-1-one,2-hydroxy-	1.65		
2-Cyclopenten-1-one,3-methyl-	0.51		
Phenol	0.96		
Phenol,2-methyl-	3.88		
Phenol,4-methyl-	0.96		
Phenol,4-methoxy-	5.59		
1,3-Propanediamine, N-methyl-	6.28		
2-Cyclopenten-1-one,3-ethyl-2-hydroxy-	1.13		
Phenol,2-methoxy-4-methyl-	0.69		
1,2-Benzenediol	4.91		
1,2-Benzenediol,3-methoxy-	2.33		
2-Methoxy-4-vinylphenol	1.03		
Phenol,2,6-dimethoxy-	4.12		
Benzoic acid,4-hydroxy-3-methoxy-	1.72		
5-tert-Butyl pyrogallol	1.13		
Phenol,2,6-dimethoxy-4-(2-propenyl)-	1.20		
Desaspidinol	1.48		

3.2. Pyrolysis reactor

After pre-processing, the remaining 9.66 tonnes/day of biomass is fed to a pyrolysis reactor which decomposes the biomass into different valuable products like bio-oil, biochar, and NCG. The pyrolysis reactor operates at 550°C and consumes 140 kW of energy. The reactor outlet contained 70.93% of the moisture in the overall bio-oil composition. The bio-oil and NCG product properties and yield are taken from the experimental results conducted by Chen et al. [9] as mentioned in Table 2. The biochar ultimate analysis has been optimized by balancing the atoms (C/H/O/N/S) across the reactor as shown in the Figure 2. It was estimated that total of 2.35 tonnes/day of biochar is being produced which contains 71.11% of C, 4.76 of H, 21.51% of O, 2.53% of N, and 0.077% of S.

3.3. Product separation

The product stream of the reactor is then passed through a cyclone separator and hot gas filter to separate the gas and solid products. A total of 2.35 tonnes/day of biochar is further cooled to atmospheric temperature releasing 19.43

kW of energy and collected as a solid product. This biochar itself is a high-density energy source that can further be modified and used for various applications.

Table 3. Bio-oil yield from condensers and separators at different temperatures

Bio-oil	Yield (wt.%)		
Components	100°C	50°C	0°C
Water	4.30	96.90	7.97
Formic Acid	0.13	0.01	1.39
Acetic Acid	2.45	0.30	14.24
2-Propanone,1-hydroxy-	1.55	0.84	1.75
Acetic acid, hydroxy-, methyl ester	0.01	0.00	0.19
1-Hydroxy-2-butanone	1.10	0.08	1.03
Furfural	0.90	0.05	1.27
Pyridine,2-methyl-	0.04	0.00	0.27
2-Furanmethanol	2.32	0.51	0.95
2-Propanone,1-(acetyloxy)-	0.40	0.00	0.66
2(5H)-Furanone	1.90	0.08	0.71
2-Cyclopenten-1-one,2-hydroxy-	3.52	0.25	0.07
2-Cyclopenten-1-one,3-methyl-	0.03	0.00	0.18
Phenol	0.62	0.14	0.20
Phenol,2-methyl-	2.71	0.04	1.34
Phenol,4-methyl-	1.10	0.04	0.24
Phenol,4-methoxy-	15.40	0.33	0.36
1,3-Propanediamine, N-methyl-	0.76	0.01	2.62
2-Cyclopenten-1-one,3-ethyl-2-hydroxy-	3.61	0.00	0.08
Phenol,2-methoxy-4-methyl-	1.05	0.00	0.18
1,2-Benzenediol	15.13	0.42	0.00
1,2-Benzenediol,3-methoxy-	8.55	0.01	0.02
2-Methoxy-4-vinylphenol	2.88	0.00	0.12
Phenol,2,6-dimethoxy-	13.03	0.00	0.31
Benzoic acid,4-hydroxy-3-methoxy-	6.58	0.00	0.00
5-tert-Butyl pyrogallol	4.28	0.00	0.00
Phenol,2,6-dimethoxy-4-(2-propenyl)-	0.06	0.00	0.4
Desaspidinol	5.6	0.00	-

After removing biochar, the 6.05 tonnes/day of remaining gas product from the hot gas filter is then condensed and separated at different temperatures using condensers and separators in series. The overall yield of bio-oil separated at 100°C, 50°C and 0°C are 7.7%, 67.5%, and 24.8%, respectively, and component-wise yield at each temperature is given in Table 3. It is observed that the first stream of bio-oil with a flow rate of 0.25 tonnes/day contains heavy components of the oil and a limited quantity of water. While the second stream with a flow rate of 2.24 tonnes/day contains primarily water and ketone compounds. The last stream having a flow rate of 0.82 tonnes/day contains remaining water and lighter phenol compounds.

3.4. NCG combustion

Finally, the NCG is compressed and passed to the burner which undergoes a combustion reaction in the presence of air to produce flue gas. Before passing the air to the burner, 253 m^3/hr of air is firstly compressed and then heated to 200°C consuming 14.8 kW of total energy. To undergo an exothermic combustion reaction, an RStoic reactor is used. The burner releases a total of 2006 m^3/hr of flue gas stream at 1567°C containing 215 kW of energy. This energy is extracted from the flue gas stream and circulated back to the pyrolysis reactor and drier and the final flue gas stream temperature comes down to 126°C.

3.5. Energy balance

The high heating value (HHV) of received biomass cotton stalk feed was estimated from the ultimate analysis as 20.2 MJ/kg [22]. After the biomass thermochemical degradation, HHV values of produced bio-oil is 20.69 MJ/kg, NCG is 14.46 MJ/kg and biochar is 26.64 MJ/kg.

The equipment-wise energy consumed or produced has been shown in Table 4. In the case of pre-processing while crushers consume 4.75 kW of energy and drier consumes energy of 67 kW which will increase if biomass is dried further. The major energy-consuming equipment in the pyrolysis plant is the reactor where all the biomass is thermally degraded at high temperatures. In the simulated plant, the reactor requires 140 kW of energy to work at 550°C. In case of separation of products, heat exchangers are required to condense the bio-oil and cool down the biochar products. The bio-oil condensers release 117 kW of energy which can be further used to heat the utility streams in the plant. Along with the condensers, a chiller is required to remove 12.3 kW of energy to condense the bio-oil to 0°C. The biochar is cooled by pneumatic conveying and air coolers releasing 19.44 kW of energy.

The simulated plant contained two compressors for the transportation of NCG and air into the burner unit consuming 2.38 kW of energy. A heat exchanger was used to heat the air to 200°C consuming 13.23 kW of energy. Combustion is an exothermic reaction that produces a flue gas containing 215 kW of energy. This flue gas is recirculated to provide heat energy to the two most energy-consuming equipment of the plant: drier and reactor.

The overall energy balance of the plant suggests that 123 kW of surplus amount of energy is remaining in the system leaving a scope of further heat integration in the plant.

Table 4. Energy requirement of equipment’s.

Equipment	Energy requirement (kW)
Crushers	4.75
Drier	67
Pyrolysis reactor	140
Bio-oil condensers	-117
Bio-oil chiller	-12.3
Biochar cooler	-19.44
Gas compressor	0.81
Air compressor	1.57
Air heater	13.23

4. Conclusion

Pyrolysis of the cotton stalk has been modelled using ASPEN Plus software to convert the waste cotton stalk into valuable products such as: biochar, bio-oil, and NCG. The bio-oil and biochar with the yield of 40% and 28% are collected and stored for further commercial applications. The NCG produced was combusted to supply heat energy to the pyrolysis reactor and drier. It was observed that the total energy balance of the plant provided 123 kW of the surplus of energy which can be consumed further to provide heat to the process utilities.

This work can further be extended from yield base modelling to rate-based modelling of pyrolysis plant for analyzing the formation of value-added products and commissioning a real pyrolysis plant based on the modeling studies.

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