Characterization of Bio-oil, Bio-char, and Pyro-gas derived from cotton stalk slow pyrolysis - as sustainable energy sources

Jinesh B Shah*,[1,2] & Janak B Valaki[3],

[1]Gujarat Technological University, Gujarat, India

[2]Atmiya Institute of Technology and Science, Rajkot, Gujarat, India

[3]Mechanical Engineering Department, Government Engineering College, Bhavnagar, Gujarat Technological University, Ahmadabad, Gujarat, India

E-mail: jinesh.shah.mech@gmail.com

The untapped energy present in this cotton stalk residue is one of the major environmental threats due to its field burning. In this research paper, slow pyrolysis process has been performed on cotton stalk having particle size 0.85 mm at 300°C, 400°C, and 500°C, at 10°C/min heating rate and 1-hour residence time. The process produced bio-oil, bio-char and pyro-gas. Physiochemical properties, GC-MS analysis, stability analysis and miscibility analysis of bio-oil have been carried out to ensure its feasibility as energy source. To ensure suitability of bio-char as soil nutrient and energy sources, its elemental analysis, metal element analysis and microscopic examination have been performed. Pyro-gas is characterized to find its suitability as energy source for heating purpose during pyrolysis process by recirculating. The maximum yield for bio-oil and Pyro-gas is 36.60 wt.% and 25.25 wt.%, respectively at 500°C, while maximum yield for char is 58.54 wt. % at 300°C. Result of physiochemical properties of bio-oil reveals remarkable variation as compare to diesel whereas GC-MS analysis found bio-oil as complex mixture. 0.02349 cst/hr. aging rate of bio-oil shows good stability at room temperature. Physiochemical properties of bio-oil vary with pure diesel causes phase separation of bio-oil and diesel during blending. Bio-oil - diesel Stabilized emulsion has been achieved by addition of 6 wt. % of *n*-butanol as co-solvent. Characterization and microscopic examination of bio-char favours usage of char as soil nutrient and energy substitute. The Pyro-gas analysis confirms its suitability as energy substitute during entire process, as it contains a substantial amount of carbon dioxide and methane.

Keywords: Bio-oil, Cotton stalk, Bio-Char, Pyro-gas, Non-edible agro residues, Sustainable fuel

Energy sector in developing countries is facing a big challenge of ensuring availability of huge energy to meet increased demand and at the same time to ensure environmental sustainability. Conventional energy sources are depleting at a rapid rate and it is estimated that it will be diminished shortly (Suganthi *et al*., 2012). This dreadful situation has motivated researchers toward exploring various opportunities and potentials for alternative and green energy sources like biodiesel, and biomass. Biodiesel derived from various biomass has gained worldwide attention in recent decades particularly for automotive applications. However, usage of plant-based bio-oils for biodiesel production is likely to adversely affect the global food chain for humans, animals and also severely affects water availability. On the contrary, biomass as energy sources has gained less attention from researchers. Agricultural biomasses are produced abundantly in India and other agriculture-dependent

countries as post-harvest agro-residues. Due to low energy content, most of the agricultural biomasses are either burnt in the farm landfills, or used for domestic cooking and industrial heating purposes. Burning of agro residues in the farm fields damages soil fertility, results in land and air pollution. Harvesting energy from these residues may prove to be a sustainable solution for the environment and entire agriculture ecosystem **(Krishna *et al*., 2016).**

Agricultural biomasses are an enriched mixture of cellulose, lignin, and hemicelluloses with a good amount of volatile matter and heating values. Its thermo-chemical characterization indicates its potential energy content. Figure 1 shows Thermo-chemical characterization of important agro residues.

As per the TIFAC (Technology Information, Forecasting and Assessment Council) 2018 Report, 5092.10 thousand tons crops are produced from cotton every year with the highest value of residue to
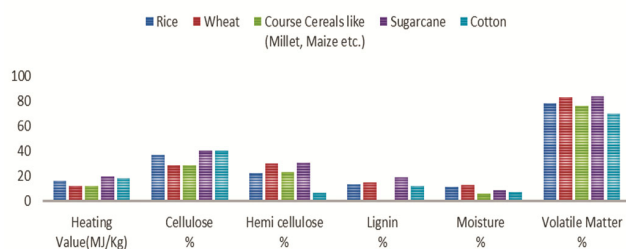
Fig. 1 — Characterization of major agro residues (Krishna *et al*., 2016)

Table 1 — Total production of agro residues in Gujarat state and its Residue to Product ratio for major crops (TIFAC, 2018)

Crop (Thousands of Ton)	Total production of agro residue in Gujarat	Residue to Production ratio (RPR)
Rice	937.41	1.76
Wheat	1654.36	1.75
Coarse Cereals like (Millet, Maize etc.)	314.66	1.5
Sugarcane	1223.15	0.3
Cotton	5092.10	3.0

product ratio as represented in Table 1. Thus looking at the thermochemical characterization, cotton residue possesses good heating value, volatile matter and less moisture. In spite of this cotton residue is a key contributor amongst all residues in Gujarat state.

Pyrolysis of Cotton Stack

Thermal Pyrolysis process is a promising technology with potential to convert the huge agricultural biomass into energy sources. It thermally decomposes biomasses into bio-oil, bio-char and pyro-gas, in absence of oxygen. (Bridgewater *et al*., 2003). Pyrolysis of cotton stalks has been investigated by some researchers. (Putun *et al*., 2005) have performed cotton stalk pyrolysis in a fixed bed reactor and investigated effect of pyrolysis temperature, gas flow rate, and particle size at heating rate of 7°C /min. Stability and miscibility issues have been observed in derived bio-oil. (Zhang *et al*., 2008) have performed pyrolysis of the cotton stalk in fluidized bed reactor under different temperatures and found that bio-oil derived through pyrolysis process can be directly used as fuel in boiler or furnace, but bio-oil upgradation is required to use it as fuel for automotive applications. (Bhavya *et al*., 2016) have reported slow pyrolysis of cotton residues at different temperatures and found maximum bio-oil yield at 400°C. Authors have noted formation of macromolecular in bio-oil that deteriorates stability and miscibility of bio-oil. (Syed

Fig. 2 — (a) Raw Cotton stalk and (b) Crushed cotton stalk

et al., 2019) had performed co-pyrolysis of cotton stalk (CS) with waste tyre (WT) and found a significant change in pyrolysis product quality but still bio-oil was facing stability issues.

Stability and miscibility of bio-oils derived from cotton residues are the main issues limiting its application as energy sources. Authors in this research work, have performed experiments with cotton stalks as biomass and investigated the energy products like Bio-oil, Bio-char and Pyro-gas generated during slow pyrolysis process

Experimental Section

Feedstock Preparation and Characterization

Sun dried cotton stalk feedstock was crushed in a crushing mill and sieved into a sieve shaking machine to get uniform particle size of 0.85 mm. Figure 2a and Figure 2b shows cotton stalk before and after pre-processing respectively. The proximate analysis was carried out according to the ASTM process using a proximate analyzer; APA 2 model (Advance Research Instruments Co., India). The instrument is precise up to furnace temperature ± 5°C with a minimum detecting capacity of 0.2%. The ultimate analysis was

performed according to the ASTM procedure using vario MICRA cube (Elementar, Germany) with oxidation and reduction temperature 850°C and 1150°C respectively. Oxygen and helium gas was used as oxidizing agent, and carrier gas during the process respectively. Fiber analysis was carried out using Van Soest method (Goering, H. K *et al*., 1970, Van Soest *et al*. 1991) using FRB-8 Fibro TRON (Tulin equipment, India). Along with feedstock composition, information regarding the decomposition pattern of feedstock is very much useful to design pyrolysis process. Thermal decomposition analysis of cotton particles was carried out using Thermo-Gravimetric analysis (TGA) at SICART Lab, V.V. Nagar, Gujarat, at a temperature range from room temperature to 900°C and at 10 °C/min heating rate.

Pyrolysis process

The slow pyrolysis process on selected cotton stalk biomass particles was performed on batch scale pyrolyzer, having a cylindrical shell made of SS 310 material with 1.28 m long, 0.28 m internal diameter and 3 mm wall thickness. The reactor shell is sealed by a lid made from SS 310 on both sides. A SS nozzle is fitted inside the shell with the provision of control for vapour inlet and outlet. A heating coil is provided longitudinally which is supported by an alumina ceramic bricks chamber of 14 gauges inside and 18 gauges outside. The maximum achievable temperature and heating rate of reactor are 1100°C with 10°C/min. For accurate measurement of temperature three temperature sensors are provided of Pt-Pt-Rh type having accuracy up to ± 2°C placed at 0.3 m apart each. Vapours generated during the pyrolysis process are drawn out using a vacuum pump which is immediately quenched in two condensers coupled in series. The process continued till the flow of vapour stopped and the reactor was allowed for cooling naturally. Bio-char yield wt. %, Bio-oil yield wt. %, and pyro-gas yield wt. % were calculated using equations 1, 2, and 3. Pyrolysis process parameters for this work are tabulated in Table 2. During each experiment, 350 g raw material was fed into the reactor. Figure 3 show Schematic diagram of the pyrolysis process. Bio-oil, Bio-char and Pyro-gas yield were calculated as per equation 1, 2 and 3.

$$\text{Bio-char Yield, wt.\%} = \frac{m_{bio-char}}{m_{feedstock}} \times 100 \ldots(1)$$

$$\text{Bio-oil Yield, wt.\%} = \frac{\begin{array}{c}(Weight\ of\ cylinder\ with\ bio-oil)- \\ (Weight\ of\ empty\ cylinder)\end{array}}{(Weight\ of\ feedstock)} \times 100 \ldots(2)$$

Pyro gas yield, wt.% =100- (bio-oil yield, wt. % + bio-char yield, wt. %)…(3)

Production of Pyrolysis products and its Characterization

Bio -Oil

Cotton stalk derived bio-oil was characterized and its composition was investigated using gas chromatography and mass spectroscopy (GC-MS) technique. Details of instruments and standards used for bio-oil characterization are tabulated in Table 3. In GC-MS technique, individual bio-oil components were separated using a GC column via volatilization
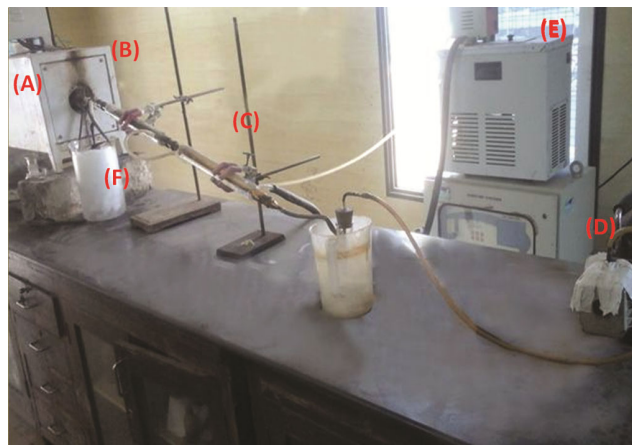

Fig. 3 — Schematic diagram of pyrolysis process. (A) Fixed Bed Reactor, (B) Reactor Outlet, (C) Glass condenser, (D) Vacuum Pump, (E) Chiller, (F) Bio-oil collecting vessel

Table 2 — Pyrolysis process parameters

Parameters	Range
Temperature	300, 400 and 500°C
Heating rate	10°C / min
Residence time	1 h
Particle size	0.85 mm

Table 3— Details of Bio-oil characterization

Characterization Methods/Properties	Standard	Details of Instruments
Moisture content	ASTM D1744	Metrohm-890 Titrando
Viscosity	ASTM D445	Anton Paar-RheolabQC
Density	ASTM D4052	METTLER TOLEDO-Densito 30PX
Flash point	ASTM D93B	Anton Paar-PMA5
Calorific value	ASTM D240	Parr-6200 Calorimeter
Ultimate analysis	ASTM Standards	Elementar-Vario MICRO cube
pH	ASTM D7946	Orion STAR Thermo Fisher Scientific
GC-MS analysis	-	Shimadzu, QP-2010

and it is identified by MS. GC-MS was performed at 300, 400 and 500ºC using HE as carrier gas by inserting 1 µL volume in a column. Major organic constituents detected during GC-MS were acids, alcohols, aromatics, esters, furans, ketones, phenols, sugars, etc. (Xiao *et al*., 2013). During bio-oil characterization, it was found that bio-oil contains a significant amount of water that deteriorates its stability by varying its viscosity with time. So, application of raw bio-oil restricts its application. Hence raw bio-oil upgradation needed to remove moisture from it. Le Zhang *et al*., 2014 proved that bio-oil stability can be improved by adding ethyl acetate in bio-oil. Thus, Moisture Free Bio-oil (MFBO) was prepared by mixing ethyl acetate and bio-oil in 1:1 proportion. The prepared mixture was mixed manually and then it was kept in steady condition for some time. After some time, there will be a separation of organic rich mixture at Top and insoluble mixture at bottom shown in (Fig. 4a). Organic rich mixture was collected and ethyl acetate

Fig. 4 — (a) Mixture of bio-oil and ethyl acetate (A) Organic rich mixture (B) Insoluble mixture and (b) Rota evaporator (A) Rota evaporator (B) bio-oil + ethyl acetate

was recovered using a Rota evaporator. Rota evaporator was operated at 40°C so that volatile matter will not be lost. 400 rpm speed and 200 Mbar vacuum pressure was set in the Rota evaporator to recover ethyl acetate as mentioned in (Fig. 4b).

Bio-oil Thermal storage stability analysis

Presence of higher oxygen, viscosity and acidity as compared to fossil fuel makes bio-oil unstable during storage. This unstable bio-oil not only degrades oil quality, but is also responsible for corrosion, erosion and carbon deposition on storage vessels when stored at high temperature (Chen *et al.* 2014). So, Thermal storage stability measures bio-oil stability in the context of viscosity at high temperature. The thermal stability of bio-oil can be measured by determining the kinematic viscosity of fresh bio-oil (V_{fresh})and viscosity of aged bio-oil (V_{aged}) (Sakthivel *et al*., 2019). Thermal storage stability was evaluated by accelerating kinematic viscosity at 80°C for 24 h that is equivalent to bio-oil storage for 1 year as stated by Osama et al 2010. Viscosity change and aging rate was calculated using equations (4) and (5).

$$\text{Change in viscosity} = \frac{V\,aged - V\,fresh}{V fresh} \times 100\,\%\ldots(4)$$

$$\text{Aging Rate} = \frac{V\,aged - V\,fresh}{24}\ \text{cst/hrs}\ldots(5)$$

If bio-oil shows remarkable change in viscosity that implies the formation of larger molecules due to polymerization. Bio-oil with a small change in viscosity and low aging rate is expected to have good thermal stability and can be stored for a longer time for further utilization.

Bio-oil miscibility analysis

Direct mixing of cotton stalk derived MFBO into diesel shows poor miscibility due to phase separation into bio-oil and diesel layers because of significant variation in its properties. To improve miscibility bio-oil is required to be upgraded using a suitable process and then to be blended. Out of many upgradation processes, Emulsification as bio-oil upgradation technique is an economical process for the preparation of bio-oil- diesel blends (Zhang *et al.* 2007). As per the directive by CANMET homogenize mixture of bio-oil- diesel blend can be made by adding additives i.e. SPAN 80, TWEEN 80, SPAN 40, etc. (Ikura *et al.,* 2003) but, bio-oil derived from different feedstocks through different processes create complications in a selection of proper additives. On the other side, the use of alcohol as a co-solvent for
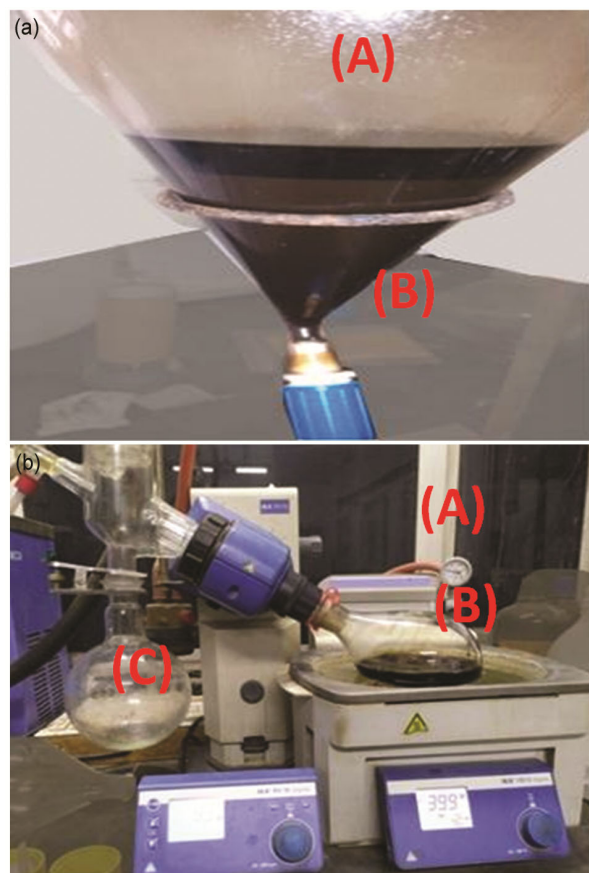
preparing bio-oil diesel blend would be a promising alternative, as alcohol has been considered as an alternative renewable fuel (Weerachanchai *et al.*, 2009). In the present work miscibility of bio-oil diesel, blends are analyzed using *n*-butanol methanol and ethanol, as it can be easily extracted from the fermentation of sugar and starch.

Bio-Char

Char, also known as bio-char or charcoal, is a solid residue produced during pyrolysis of biomass. Elemental and metal characterization along with Scanning Electron microscopic (SEM) analysis are performed at various temperatures. Details of Bio-char characterization are shown in Table 4.

Pyro-gas

Pyro gas produced during the pyrolysis process contains a significant amount of heating value. It can be used as a carrier gas to make the entire process thermally balanced. Generated gas at various temperatures was allowed to pass through a gas analyzer for its characterization. Gas composition was analyzed for 300, 400 and 500°C. Generated pyro-gas was allowed to pass through a gas column that determined gas composition in terms of CO, CO_2, CH_4 and H_2. For accuracy purpose reading was taken at every 10-minute interval and average of combined result was considered.

Result and Discussion

Analysis of Prepared Cotton Feedstock

Results of proximate analysis, ultimate analysis, and fiber analysis of cotton stalks are summarized in (Table 5). The higher value of the volatile matter in proximate analysis is an indication of high conversion capacity of bio-oil, while higher value of fixed carbon indicates higher amount of char. The results obtained through ultimate analysis are used for calculating heating values. Fiber analysis of cotton stalks shows that cellulose and hemicellulose contents are 65-70% of total constituent matter, while lignin content is 30-35 %. From this data, it can be predicted that a minimum of 30% biomass will remain as residue at the end of pyrolysis process because the decomposition of lignin starts at a higher temperature. Result of TGA in Figure 5 shows that effective weight loss starts at 300°C and almost 73% of feedstock decomposition completes at 500ºC. It is suggested to perform pyrolysis processes at temperatures 300, 400, and 500 ºC.

Pyrolysis process Yield

The results of the process yield are shown in Table 6. The pyrolysis process was operated at 300, 400, and 500°C. (Table 3) shows wt. % yield of bio-oil, bio-char, and pyro-gas from cotton stalk. It can be revealed from Table 6 that (1) Temperature and bio-oil yield shows linearly relation with the increase in temperature. Bio-oil yield increased with temperature and it was maximum at 500°C with 36.60 wt. % yield. (2) Gas follows the same trend as bio-oil. (3) While with an increase in temperature, char yield

Table 4 — Details of Bio-char characterization

Bio-char properties /Characterization methods	Details of Instrument/Methods
Ultimate analysis	Elementar-Vario MICRO cube
pH	Filter treatment
Ash	Gravimetric analysis
Volatile matter	Gravimetric analysis
Metal characterization	Plasma optical spectrometry
Scanning Electron Microscopes	Jeol Jsm 7100f

Table 5 — Feedstock Analysis

Particular	Property	Unit	Cotton stalk	Applied method	Instrument used
	Moisture	wt.%	6.59	ASTM E871	
	Volatile matter	wt.%	78.695	ASTM E 872	APA 2 model
Proximate analysis	Ash content	wt.%	1.665	ASTM D1102	
	Fixed carbon	wt.%	13.05	ASTM E 777	
	C	wt.%	43.32	ASTM D-3178	
Ultimate analysis	H	wt.%	5.175	ASTM D-3178	vario MICRA cube
	N	wt.%	1.63	ASTM D-3179	
	S	wt.%	0.02	ASTM D-3177	
	O*	wt.%	51.485	ASTM D-3177	
	Lignin	wt.%	32.1		
Fiber analysis	Cellulose	wt.%	38.68	Van soest	FibroTRON
	Hemicelluloses	wt.%	25.51		
	HHV	MJ/Kg	17.48	ASTM-D4809	Parr-6200 Calorimeter
	H/C	--	1.42		
	C/O	--	1.12		
	H/O	--	1.59		
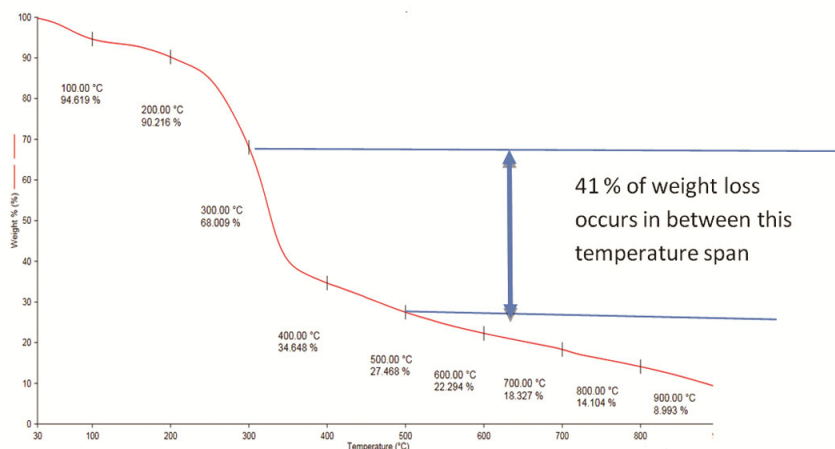
Fig. 5 — Thermo Gravimetric Analysis (TGA) of cotton stalk pyrolysis process

Table 6 — Pyrolysis Process yield			
Bio Products	wt. % Yield (300 °C)	wt. % Yield (400 °C)	wt. % Yield (500 °C)
Bio-oil	31.66	34.84	36.60
Char	58.54	47.72	37.78
Gas*	57.32	17.43	25.25
* By difference			

decreases eventually. The influence of temperature on cotton stalk pyrolysis follows the same trend as reported in previous literature (Pütün *et al.*, 2005, Zheng *et al.*, 2008, Ali *et al.*, 2015, Wang, X., 2016, Xie, Y *et al.*, 2019).

Analysis of Pyrolysis products

Bio-oil

Results of the Bio-oil characterization and its comparison with pure diesel are shown in Table 7. The energy density of bio-oil is 22.01 MJ/Kg that is greater than the feedstock. Bio-oil composition shows the presence of S, N, and other pollutants compounds in small concentrations. The results of viscosity, density, and gross heating value of bio-oil and diesel reveal considerable variation that restricts its direct use as fuel while the presence of oxygen in higher amounts confirms the requirement of bio-oil upgradation.

Results of GC-MS of bio-oil produced at 500°C are shown in Table 8. GC-MS analysis of bio-oil shows that bio-oil is a mixture of complex compounds mainly consisting of phenol, ketenes and carboxylic acid, etc. During GC-MS, it was found that presence of phenol about 1- 4 wt.% and furans 2-8 wt.% reveal bio-oil as very valuable energy source.

Thermal Storage Stability Analysis of Bio-Oil

Stabilization of bio-oil is a major concern before it is further used. As discussed earlier, kinematic

Table 7 — Moisture free Bio-oil characterizations and its comparison with pure diesel		
Properties	Bio-oil (500°C)	Pure diesel
Moisture content (wt. %)	< 0.1	-
Viscosity (cst)	4.638	2.82
Density (Kg/dm^3) at 28.2 °c	0.9778	0.824
Flash point (°C)	40	44
Gross heating value (MJ/Kg)	22.0158	44.99
C%	50.20	90.02
H%	5.985	9.63
N%	1.10	0.07
S%	0.38	0.00
O%*	42.33	0.28
pH	2.91	4.64
H/C molar Ratio	1.42	1.28
C/O molar Ratio	1.57	444.54
H/O molar Ratio	2.24	570.67
* By Difference		

viscosity of fresh MFBO was measured and then, fresh bio-oil was placed in a furnacefor 24 h at 80°C to accelerate the aging process. After that its kinematic viscosity needs to be measured (Chen et al, 2014). Kinematic viscosity of fresh MFBO and aged MFBO was measured at 40°C by Anton Paar-Rheolab QC viscometer. The results of the kinematic viscosity and aging rates are tabulated in (Table 9). The obtained results indicate no significant change in viscosity of fresh bio-oil and aged bio-oil. Aging rate of 0.02349 cst/hr of MFBO shows good thermal storage stability. This, in turn, signifies that MFBO can be stored for a longer period.

Miscibility analysis of Stabilized Bio-oil

Various blends of stabilized bio-oil-diesel were prepared by adding ethanol, *n*-butanol, and methanol as co-solvent in different proportions. The prepared

Table 8 — GC-MS result of Cotton stalk at 500 °C

Peak	Retention time	Area%	TIC Name	Functional group
1	13.67	1.68	Phenol, 4-Ethenyl-2,6-Dimethoxy-	Phenol
2	10.399	1.73	1,4:3,6-Dianhydro-.Alpha.-D-Glucopyranose	Sugar
3	7.479	1.77	2-Cyclopenten-1-One, 3-Methyl-	Ketone
4	11.441	1.77	2-Methoxy-4-Vinylphenol	Phenol
5	3.457	1.81	Propanoic Acid	Carboxylic acid
6	6.717	1.98	Butyrolactone	Carboxylic acid
7	5.641	2.13	Benzene, Chloro-	Phenol
8	8.295	2.57	1,2-Cyclopentanedione, 3-Methyl-	Ketone
9	8.943	2.59	Phenol, 3-Methyl-	Phenol
10	5.87	2.69	2-Furanmethanol	Furan
11	9.052	3.32	Phenol, 2-Methoxy-	Phenol
12	11.778	4.06	Phenol, 2,6-Dimethoxy-	Phenol
13	5.438	7.54	2-Furancarboxaldehyde	Aldehydes

Table 9 — Viscosity change and aging rate of MFBO

Particular	Result
Viscosity of fresh bio-oil (cst)	4.638
Viscosity of aged bio-oil (cst)	5.2018
Change in viscosity	0.5638
Aging rate (cst/hr.)	0.02349

Table 10 — Stabilized Bio-oil miscibility analysis results

Sr. No	Bio oil (Wt. %)	Diesel (Wt. %)	Co-solvent (Wt. %)	Remarks
1	10%	89%	1% - Ethanol	0 hours miscibility
2	10%	89%	1% - n-Butanol	0 hours miscibility
3	10%	89%	1% - Methanol	0 hours miscibility
4	10%	88%	2% - Ethanol	0 hours miscibility
5	10%	88%	2% - n-Butanol	0 hours miscibility
6	10%	88%	2% - Methanol	0 hours miscibility
7	10%	87%	3% - Ethanol	0 hours miscibility
8	10%	87%	3% - n-Butanol	0 hours miscibility
9	10%	87%	3% - Methanol	0 hours miscibility
10	10%	86%	4% - Ethanol	0 hours miscibility
11	10%	86%	4% - n-Butanol	0 hours miscibility
12	10%	86%	4% - Methanol	0 hours miscibility
13	10%	85%	5% - Ethanol	0 hours miscibility
14	10%	85%	5% - n-Butanol	0 hours miscibility
15	10%	85%	5% - Methanol	0 hours miscibility
16	10%	84%	6% - Ethanol	More than 7 days miscibility
17	10%	84%	6% - n-Butanol	0 hours miscibility
18	10%	84%	6% - Tween 80	0 hours miscibility
19	20%	74%	6% - n-Butanol	Moe than 7 days miscibility
20	30%	64%	6% - n-Butanol	More than 7 days miscibility

emulsions were kept under observation for 24 hours. In case of mixture showing phase separation within 24 hours, then the quantity of co-solvent was changed. Experimentation was started by adding 1 wt. % co-solvent, 10 wt. % stabilized bio-oil and 89 wt. % diesel. Stabilized oil-diesel blends show poor miscibility with ethanol and methanol up to 6% wt. while stabilized oil- diesel emulsion miscibility was achieved by addition of 6% n-butanol up to 30% as tabulated in (Table 10) and prepared emulsion was kept under observation for more than 7 days. Results of miscibility are shown in (Figure 6). Miscibility results were triplicate to ensure consistency of results. Energy was not utilized for the preparation of blends.

Analysis of Bio-Char

Results for elemental analysis of bio-char are tabulated in (Table 11). The results show presence of heating value and important chemical elements. It is an indication for its suitability as soil nutrient and heating elements for industrial heating applications like coal. It can be seen from the results that wt. % of C, wt. % of N & wt. % of S increases with temperature while wt. % of H and wt.% of O decrease simultaneously. To use char as soil nutrient higher wt. % of C is favorable, while value of other elements should be as minimum as possible. so looking to this, Quality of char is good at 500°C. The results of elemental analysis are inline to the findings of (Al Afif *et al.*, 2020, Poudel *et al.*, 2015,). Ash % and pH value in bio-char increase with temperature whereas volatile matter decreases with rise in temperature, that

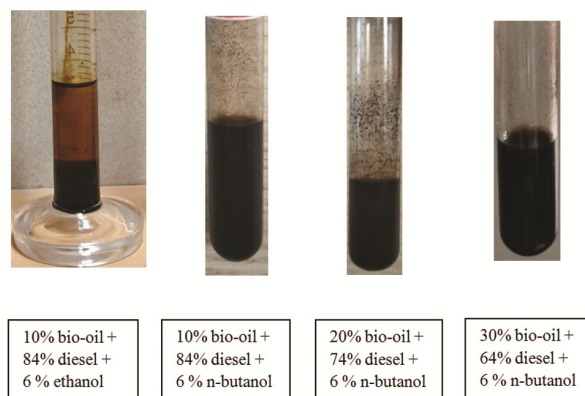| 10% bio-oil + 84% diesel + 6 % ethanol | 10% bio-oil + 84% diesel + 6 % n-butanol | 20% bio-oil + 74% diesel + 6 % n-butanol | 30% bio-oil + 64% diesel + 6 % n-butanol |

Fig. 6 — StabilizedBio- oil miscibility with diesel

Table 11 — Elemental analysis of cotton stalk bio-char

Property	0°C	300°C	400°C	500°C
C (%wt.)	43.42	61.30	64.49	65.72
H (%wt.)	5.175	2.49	2.08	1.71
N(%wt.)	0	0.87	1.07	1.08
S (%wt.)	0.02	1.06	1.08	1.14
O *(%wt.)	51.405	35.34	32.36	31.39
LHV (MJ/Kg)	17.51	20.73	21.34	21.44
H/C ratio	1.42	0.48	0.38	0.30
O/C ratio	0.89	0.43	0.37	0.35
pH	7.86	8.80	9.30	9.67
Ash content (%wt.)	1.66	7.05	9.95	13.02
Volatile matter (%wt.)	78.69	72.65	63.12	54.36

*Calculated by difference
LHV calculated using following empirical equation (Sheng *et al.*, 2005)
LHV=-1.3675+0.3137C+0.7009H+0.0318O

Table 12 — Bio-char metal element analysis

Metal (mg/Kg)	0°C	300°C	400°C	500°C
Cu	3.70	1.63	1.70	1.75
Zn	8.71	3.25	2.29	2.21
Pb	2.30	1.21	1.05	0.80
Ni	3.27	2.21	1.86	1.54
Cr	14.55	2.54	2.21	1.85
Mn	4.29	1.65	1.15	0.86

is because, at higher temperature rise in wt. % of C favours generation of ash and decreases volatility of material ((Younis *et al*, 2017). Table 12 represents the presence of metallic elements in cotton stalks at different temperatures. Results of metal element analysis shows decreasing trend as compared to cotton stalk with rise in temperature that is due to at higher temperature metal could be immobilized into bio-char. This type of trend suggests low environment risk as soil amendments (Wang et al, 2018). Looking at all elemental values of char favours its suitability as a soil nutrient. Effect of temperature and other parameters on char are analyzed through surface morphology using scanning electron micrographs (SEM). (Fig. 7) shows SEM images of cotton stalk char particles at different temperatures. Char micrographs reveal the presence of pores. Char micrographs at 300°C show the presence of filled tissue due to incomplete volatilization leaving non-developed pores. However, char particles at 400°C and 500°C clearly show the presence of cracks, shrinkages, and pores. It can also be seen that at a higher temperature, the particle structure becomes more ordered. The properly arranged pore structure of char possesses high BET surface area and good absorptive capacity (Guo, J *et al*., 1998).

Analysis of Pyro-Gas

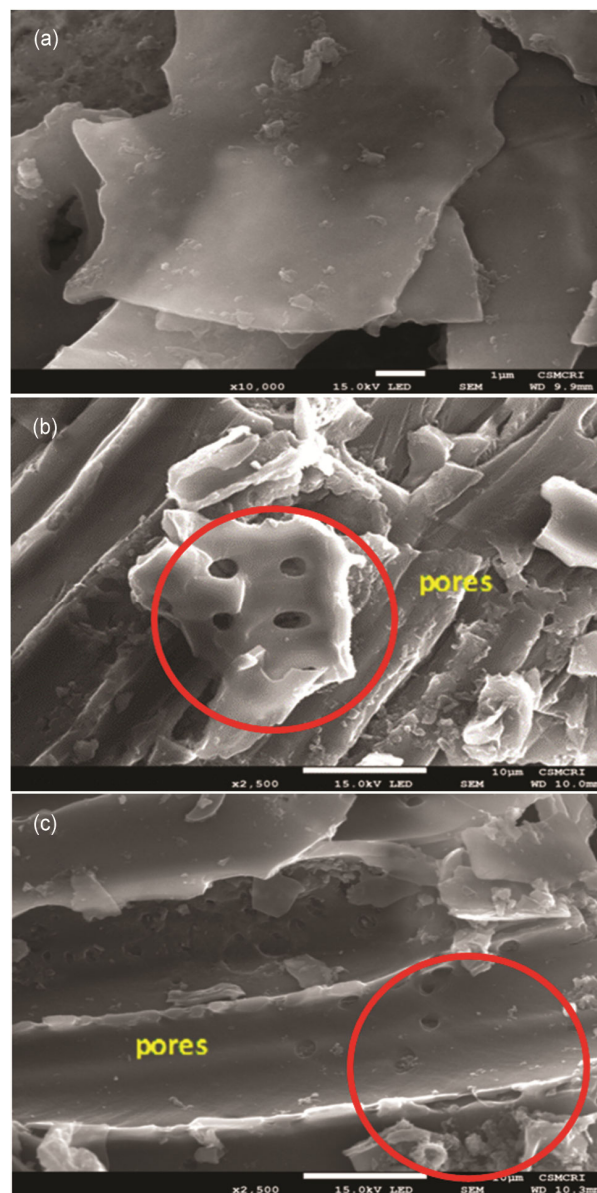Pyro-gas analysis was carried out to confirm its suitability as a carrier gas during the pyrolysis process

Fig. 7 ─ SEM of Cotton stalk bio-char (A) at 300 °C, (B) at 400 °C, (C) at 500 °C

Table 13 — Pyro-Gas Analysis

Gas	300°C	400°C	500°C
Carbon monoxide (CO, wt. %)	8.32	6.52	4.33
Carbon dioxide (CO_2 wt. %)	40.42	33.25	27.36
Methane (CH_4 wt. %)	4.32	8.22	10.24
Hydrogen (H_2 wt.%)	0.26	0.35	0.54

using a gas analyzer. Pyro-gas was analyzed at 300, 400 and 500 °C reaction temperature. Reading was taken at every 10-minute interval. Gas produced during pyrolysis of the cotton stalk was a mixture of Carbon Monoxide (CO), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2) etc. The average wt. % of different gas is tabulated in (Table 13). It can be seen

that produced gas mainly contains carbon dioxide, carbon monoxide and methane in major proportion due to decarbonylation. While, hydrogen was present in very small proportions due to cracking reactions. Overall decreasing trend was observed in CO that is due to decarbonylation at low temperature and similar trend was observed in CO_2 due to production of carbonyl and carboxylic group. While an overall increasing trend was observed in Methane and hydrogen. Rise in hydrogen due to aromatic condensation and thermal cracking whereas rise in methanedue to decomposition of methoxyl and methylene at elevated temperature (Cheng *et al.*,2021). The same trend was observed by (Yang *et al.*, 2007, Sarkar, J. K *et al.*, 2020). As pyro-gas contain a significant amount of CH_4 at 500°C along with some other gases. That reveals its suitability as carrier gas during the pyrolysis process for heating purposes.

Conclusion

Results of this research work reveal that non-edible agro residues like cotton stalk can be used as feedstock for extraction of energy in various forms like Bio-oil, Bio-char, and Pyro-gas. Following are the key conclusions from research work.

1. Non-edible agro residues of cotton stalk produced energy byproducts like Bio-oil, Bio-char, and Pyro-gas when pyrolyzed using batch pyrolysis process with a maximum yield of 36.60 wt. %, 58.54 wt. %, and 25.25 wt. % respectively.

2. Bio-oil characterization and GC-MS results show that bio-oil is a mixture of complex compounds. The physio-chemical properties of bio-oil show quite dissimilarity in comparison to diesel. So bio-oil upgradation is needed before blending it with diesel. However, the miscibility of bio-oil diesel can be complied up to B10, B20, and B30 once it is upgraded via emulsification by addition of 6 wt. % of n-Butanol.

3. Cotton stalk-derived bio-oil contains 0.02349 (cSt/hr.) aging rate which reveals good thermal storage stability.

4. Elemental analysis of bio-char reveals its suitability as energy substitute, while metallic characterization and results of scanning micrographs strengthen its suitability as soil nutrient at moderate temperature due to low environment risk.

5. Elemental analysis shows that the major part of pyro-gas was covered by CO_2 and methane gas,

which indicates its suitability for recycling as carrier gas for pyrolysis process.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The authors declare that data supporting the findings of this study are available within the article.

References
1 Bridgwater, *Chem Eng J*, 91 (2003) 87–102.
2 Al Afif R, Anayah S S & Pfeifer C, *EDP Sci*, 116 (2019) 1.
3 Al Afif R, Anayah S S & Pfeifer C, *Renew Energy*, 147 (2020) 2250.
4 Al Afif R, Pfeifer C & Pröll T, *Biomass Bioenerg*, 120 (2019) 281.
5 Cheng J, Hu S C, Sun G T, Geng Z C & Zhu M Q, *Biomass Bioenergy*, 7 (2021) 187.
6 Chen D, Zhou J, Zhang Q & Zhu X, *Renew Sust Energy Rev*, 40 (2014) 69.
7 Dhyani V &Bhaskar T, *Renew Energy*, 129 (2018) 695.
8 Diebold J P &Czernik S, *EnergyFuels*, 11 (1997) 1081.
9 Goering H K & Van Soest P J, Forage fiber analyses: apparatus, reagents, procedures, and some applications (No. 379). Agricultural Research Service, US Department of Agriculture (1970).
10 Guo J & Lua A C, *J Anal Appl Pyrol*, 46 (1998) 113.
11 Ikura M, Stanciulescu M & Hogan E, *Biomass Bioenerg*, 24 (2003) 221.
12 Jahirul M I, Rasul M G, Chowdhury A A & Ashwath N, *Energies*, 5 (2012) 4952.
13 Karthik A, Hussainy S A H & Rajasekar M, *Int J Curr Microbiol App Sci*, 9 (2020) 459.
14 Krishna B B, Biswas B, Kumar J, Singh R & Bhaskar T, *Waste Biomass Valori*, 7 (2016) 71.
15 Lédé J, Broust F, Ndiaye F T & Ferrer M, *Fuel*, 86 (2007) 1800.
16 Maity S K, *Renew Sust Energy Rev*, 43 (2015) 1446.
17 Oasmaa A & Kuoppala E, *Energy Fuels*, 17 (2003) 1075.
18 Oasmaa A &Peacocke C, (2010). *Properties and fuel use of biomass-derived fast pyrolysis liquids*. VTT Publications: Finland, 731 (2010) 79.

19 Poudel J, Ohm T I, Lee S H & Oh S C, *Waste Manag*, 40 (2015) 112.

20 Pütün A E, Özbay N, Önal E P & Pütün E, *Fuel Process Technol*, 86 (2005) 1207.

21 Sakthivel R, Ramesh K, Shameer P M &Purnachandran R, *J Energy Inst*, 92 (2019) 768.

22 Sarkar J K & Wang Q, *Biomass Processes*, 8 (2020) 837.

23 Schaffer S, Pröll T, Al Afif R & Pfeifer C, *Biomass Bioenerg*, 120 (2019) 281.

24 Schmidt H P, Pandit B H, Cornelissen G & Kammann C I, Biochar-based fertilization with liquid nutrient enrichment: 21 field trials covering 13 crop species in Nepal. Land Degradation & Deve, https://doi.org/10.1002/ldr.2761, (2017).

25 Shafiee S &Topal E, *Energy Policy*, 37 (2009) 181.

26 Shah S A Y, Zeeshan M, Farooq M Z, Ahmed N & Iqbal N, *Renew Energy*, 130 (2019) 238.

27 Sheng C &Azevedo J L T, *Biomass Bioenerg*, 28 (2005) 499.

28 Sriram N &Shahidehpour M, *Renew Biomass Energy*, (2005) 612.

29 Suganthi L & Samuel A A, *Renew Sust Energy Rev*, 16 (2012) 1223.

30 Van Soest P V, Robertson J B & Lewis B A, *J Dairy Sci*, 74 (1991) 3583.

31 Venkatesh G, Venkateswarlu B, Gopinath K A, Srinivasrao C, Korwar G R, Reddy B S &Venkanna K, Indian J *Dryland Agricult Res Dev*, 28 (2013) 48.

32 Wang Z, Shu X, Zhu H, Xie L, Cheng S & Zhang Y, *Environ Technol*, 41 (2018) 1347.

33 Weerachanchai P, Tangsathitkulchai C & Tangsathitkulchai M, *EngTechnol*, 56 (2009) 387.

34 Xiao R & Yang W, *Renew Energy*, 50 (2013) 136.

35 Xie Y, Zeng K, Flamant G, Yang H, Liu N, He X & Chen H, *Energy*, 179 (2019) 1124.

36 Yang H, Yan R, Chen H, Lee D H & Zheng C, *Fuel*, 86 (2007) 1781.

37 Younis U, Athar M, Malik S A, Bokhari T Z & Shah M, *Adv Environ Res*, 6 (2017) 127.

38 Zhang L, Shen C & Liu R, *Front Energy Res*, 38 (2014) 045001.

39 Zhang Q, Chang J, Wang T & Xu Y, *Energy Convers Manag*, 48 (2007) 87.

40 Zheng J L, Yi W M & Wang N N, *Energy Convers Manag*, 49 (2008) 1724.