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A Comprehensive Review on Feasibility of Different Agro Residues for Production of Bio-Oil, Bio-Char and Pyro-Gas

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ABSTRACT

Burning of post-harvest non-edible agro residues (biomass) are the major source of environmental and soil pollution, affecting the lives of millions of people, especially in certain demography of developing countries like India. Non edible agro residues contain toxic structural constituents, making it unsuitable for cattle feed. However, due to its cellulosic and lignocellulosic constituents, it has the potential to be used as a promising feedstock to develop value added energy products. Authors in this review paper have comprehensively reviewed the technological aspects related to conversion of agro residues into value added energy products like bio-oil, bio-char, and pyro gas. Various non-edible agro residues like Cotton stalk, castor stalk, Maize stalk, Rice straw, Rice husk, Corn cob, Sugarcane bagasse, and wheat straw etc., have been reviewed for its potential as feedstock material for thermo chemical conversion to obtain energy products like bio-oil, bio-char, and pyro-gas. Different physio-chemical properties, its chemical characterization methods, different bio-oil upgradation techniques, Techno-economic analysis (TEA), and Life Cycle Assessment (LCA) have been reviewed for different thermo-chemical conversion processes. The reviewed works reveal that byproducts derived from pyrolysis of non-edible agro residues have potential to be used as biofuels. Bio-oils after upgradation may be used as fuel, bio-char with appropriate pulversing may be used as soil nutrient, and pyro-gas may be used as energy gas or carrier gas for process industries. LCA of different processes for different agro residue-based biofuels indicate that conversion of biomass into energy fuels is an sustainable, and economical solution for the environment point of view and economic point of view through pyrolysis process as compare to the other conversion processes because pyrolysis process can accommodate agro waste and produce bio-char and pyro-gas along with bio-oil having capacity to generate good revenue.

Keyword: Biomass; pyrolysis; bio-oil upgradation; sustainable biofuels; life cycle assessment

INTRODUCTION

Due to remarkable economic development and higher penetration of inclusive growth patterns throughout the world in the last 20 years, the energy demand and hence, the usage of fossil fuels have increased rapidly and reached its highest level in the history of mankind. However, as per the report of IEA (International Energy Agency), fossil fuels like oil, coal, and gas resources will be available only for 35,107 and 37 years respectively. The projected availability of these resources will be up to 2053, 2125 and 2055 (Shafiee et al. 2009). Moreover, increased usage of these resources will not only diminish fuel resources, but also create adverse impacts on environment, human health, and global climate change. The world has already started experiencing the most brutal reply from Mother Nature. It is a soaring time to think about climate change, environmental, and ecological impacts due to usage of fuels. Nevertheless, we have to literally act upon the solutions at multiple fronts.

One of the directions to fulfill the present and future energy demands and simultaneously ensuring sustainability of the fuels and its usage, renewable energy sources have been considered as favorable energy sources (Farhad et al. 2008).These energy sources are continuously being refilled by nature and derived directly from the nature in form of sun, wind, geothermal, tidal etc., making these sources sustainable, environmentally friendly, efficient and economically viable (Ellaban et al. 2014; Mata et al. 2010). Since last decades, another shift has been witnessed for using bio-based energy sources, which have been proved as the viable, environmentally friendly, and sustainable sources of energy. In general, liquid and gas fuel derived from biomass is broadly known as biofuels. (E.g. methanol, ethanol, biodiesel, bio-oil, FT (Fisher Tropsch) diesel) (bahadar et al. 2013; demirdas et al. 2010).

BIOMASS IN INDIAN CONTEXT

India is the 7th largest country in the world with great biodiversity and mainly agriculture-based economy. Approximately 400-500 million tons of agro residue-based biomass is produced every year. It offers a huge scope of energy harvesting compared to other renewable sources (Dubey et al. 2009). In developing and underdeveloped countries, due to poor availability of energy, these residues are used for burning through direct combustion for cooking and heating purposes. Instead of less efficient direct combustion, thermo-chemical conversion processes are more efficient and promising alternatives (Singh et al. 2010). Various government bodies like MNRE (formerly known as MNES), prominent academic institutions like Indian Institute of Science (IISc), Indian Institutes of Technology (IITs) etc. are putting lots of effort into utilizing the agro waste of these energy sources.

INDIAN BIOFUELS POLICIES

The Indian Government started the Ethanol Blending Petroleum Program (EBPP) in 2003, under the vision of petroleum blending with biofuels. As per the recommendation of the Ministry of New and Renewable Energy (MNRE) for blending of ethanol up to 20 % in 2017, ethanol requirement will increase to 3.4 billion liters by 2020 (Basavaraj et al. 2013). In India, sugarcane is mainly used for ethanol production and it is expected that its cultivation is to be increased by 20-30% of the current sugarcane harvest. As the sugarcane crop demands huge amounts of water compared to other crops, the ethanol and subsequent production of biofuel from sugarcane requires a huge quantity of water and land that already is heavily exploited (Fraiture et al. 2008).

AVAILABILITY OF AGRO RESIDUE AND ITS IMPACT

India being an agriculture-based economy, availability of crop residues is available substantially throughout the year. Table 1 shows production data of crop wise agro based residues in India.

TABLE 1. Crop wise residue generated in India

Crop residues	Production in 1994 (Million Tons) (Jain et al. ,2014)	Production in 2010 (Million Tons) (Jain et al. ,2014)	Production in 2018 (Million Tons) (TIFAC Report-2018)
Rice straw	103.48	159.98	225.487
Wheat straw	19.42	17.77	145.449
Maize stalks	0.36	0.40	27.880
Cotton stalks	19.39	30.79	66.563
Soybeans stalks	12.87	34.87	27.780
Sugar cane tops	68.12	117.97	119.16
Groundnut straw	19.00	23.16	12.900
Total	242.64	384.94	625.219

Figure 1 shows the contribution of different agro residues in air pollution. It indicates that major contributing agro residues in air pollution are rice (40%), wheat (22%), sugarcane (20%) and cotton (8%). Because burning of crop residues leads to many adverse impacts on human health by releasing soot, GHG emission of different gasses responsible for global warming; deteriorate plant nutrient and soil fertility. Hence, it is immensely important to address these issues and find a sustainable solution.

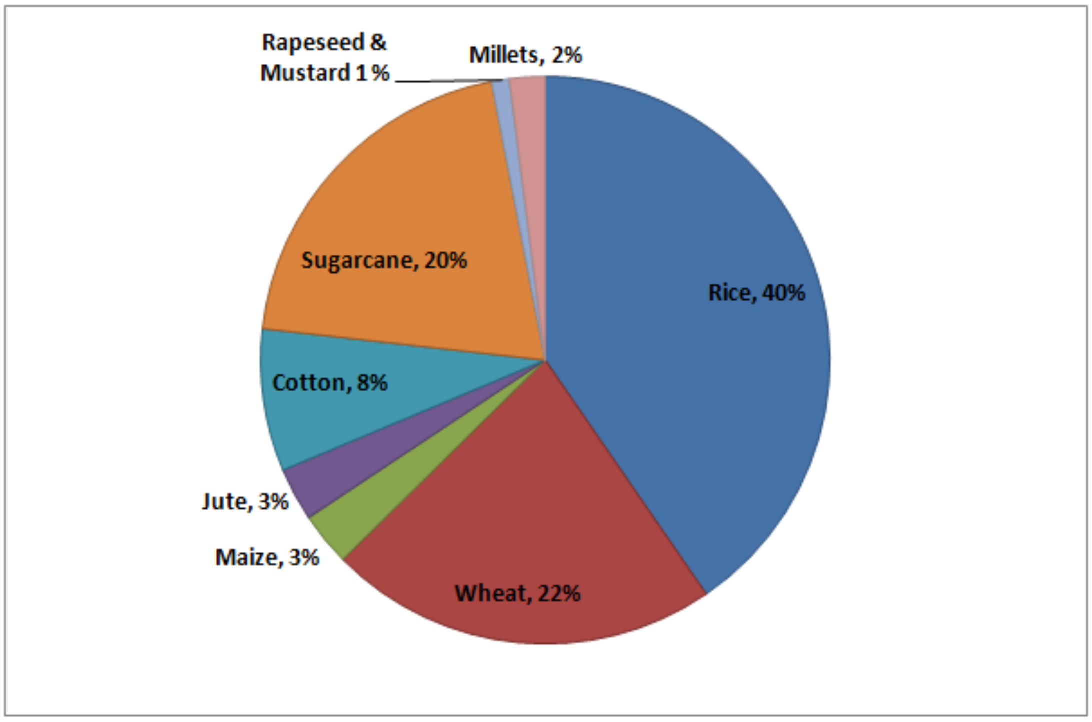

FIGURE 1. Contribution of crop residues in GHG Emission

CONVERSION OF BIOMASS

BIOMASS CONVERSION TECHNOLOGIES

Thermo-chemical processes and Bio-chemical processes are the two main technologies which may be used for conversion of biomass into biofuel. However, application of Bio-chemical processes for conversion of agro residues is less efficient and uneconomical technology due to various technical limitations like low bulk density, high enzyme cost, high viscosity substrate and low ferment ability of some substrate. On the contrary, the thermo-chemical process is more efficient and economical, due to less process steps, low processing time and high quality bio-products (Chen et al. 2012). Thermo-chemical conversion process is the process that converts bio-mass into end product through the application of heat in two approaches. In the first approach, bio-mass is converted into gaseous form through combustion or gasification, while the second approach is to liquefy bio-mass at high pressure or high temperature (Pandey et al. 2015; Bridgewater et al. 2003) Table 2 shows comparison between different thermo- chemical conversion processes. Biomass conversion process should be selected based on parameters like type of bio-mass, requirement of end product, environmental standards, etc. Different thermo-chemical conversion processes are shown in Figure 2.

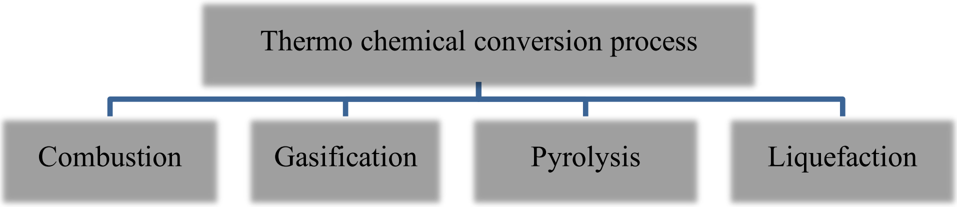

FIGURE 2. Various Thermo Chemical Conversion Processes

TABLE 2. Comparative analysis of thermo-chemical conversion processes for Biomass (Shah et al. 2019)

Parameters	Thermo-Chemical conversion processes for biomass				Further Scope
	Combustion	Gasification	Pyrolysis	Liquefaction	
Temperature	>300 ° C	700-1500 ° C	350-800 ° C	250-400 °c	-----
Pressure	Atmospheric	Atmospheric	Atmospheric	50-200 MPa	Since liquefaction process is carried out at high pressure leads to increase process cost. So further research is required on reduction in pressure.
Primary product	Heat	Syngas	Bio-oil, Syngas, Bio-char	Bio-oil, Syngas, Bio-char	Further research is required for fruitful usage of end product from all thermo-chemical conversion process
% of yield	Avg. 20MJ/ one kg of dry biomass	Heating value of gas 6-19 MJ/m^3	60-75 % (Fast pyrolysis)	20-60 %	Technological advancement is required for optimum % of yield from biomass.
Biomass	Wood or any plant	Anything with organic content can be gasified	Biomass < 10 % moisture content	Algae, sewage, Animal manure etc.	Further technological up-gradation is required to remove barrier in selection of biomass
Moisture content	Up to 65 %	5-30 %	10-20 %	No limitation	Strong technology is required for removal of moisture content from biomass.
Limitations	Fouling and corrosion on combustor make limited usage of this process.	Clinkering problem due to increase in oxidation temperature make its usage limited in industry	Presence of Highly oxygen content and moisture content create immiscibility of bio-oil with hydrocarbon fuel.	As this process is mainly for 3rdgeneration of biomass whose resource availibity is very limited.	Further advancement is required to remove limitation of all thermo-chemical conversion process

As transportation of bulky solid residue is costly, a suitable technology for conversion of solid crop residue into liquid is a matter of research. (R. Zanzi et al. 1996). Pyrolysis is one of the important thermo-chemical processes that decompose solid biomass in the absence of oxygen and produces vapors, which on condensation, produces bio-oil. Bio-char and pyro-gas are produced along with bio-oil as byproducts. Application of end products from pyrolysis shown in table 5.

TABLE 3. Applications of Bio-oil, Bio-char, and Pyro-gas (Goyal et al. 2008)

Bio -Oil	Bio-Char	Pyro-Gas
• Combustion fuel, Transportation fuel, Power generation • AS preservatives, e.g., wood preservative. • As adhesives.	• Briquettes as high efficiency fuel for industrial heating for process industries. • For production of carbon Nano tubes. • Used in gasification process for generation of hydrogen by thermal cracking as fertilizer.	• As fuel during combustion process, due to presence of carbon dioxide along with methane.

Various types of pyrolysis processes as shown in Figure 2, have been developed to enhance conversion rate, conversion efficiency, product yield, and produce other byproducts. However, slow, fast, and flash pyrolysis are mainly used for crop-based residues. Slow pyrolysis is performed using low heating rate, low temperature, and longer residence time which favors production of bio- char. Fast pyrolysis is performed at moderate temperature, high heating rate, and comparatively short residence time of the vapor which favors production of bio-oil. Flash pyrolysis process requires very low residence time (For a few seconds or even less than that) and very high heating rate and it favors formation of pyro-gas. As this process is carried out at a high heating rate, particle size of the residues should be small (Goyal et al. 2008).

This review article is an attempt to check feasibility of pyrolysis process for production of bio-oil, bio-char and pyro-gas from selected crop residues i.e. sugarcane, maize stalk, cotton stalk, rice straw, wheat straw etc. in Indian context for technological, economic and environmental point of view.

VARIOUS FEEDSTOCK

Selected biomass needs to be analyzed before it is used as feedstock in the pyrolysis process for determining the reaction conditions, and predicting the product behavior.

Various types of feedstock analysis required to be performed on biomass before applying pyrolysis process, are tabulated in Table 4 with its ASTM standards. Feedstock analysis of selected bio mass represented in Table 5.

TABLE 4. Pre-process feedstock analysis

Sr. No	Feed-stock analysis	ASTM Standard	Importance	Accepted Range	References
1	Moisture	ASTM E871	It is desirable to have lower moister content in bio mass.	0-20	(Dhyani et al. 2018, Lim et al. 2016, Akhtar et al. 2012)
2	Volatile matter	ASTM E872	High volatile matter means bio mass can ignite at low temperature.	0-80	(Dhyani et al. 2018, Lim et al. 2016, Akhtar et al. 2012)
3	fixed carbon	ASTM E777	High fixed carbon leads to production of high Bio char.	0-25	(Guedes et al. 2017, Dhyani et al. 2018; Lim etal. 2016, Lehto et al. 2013, Jacobson et al. 2013)
4	Ash	ASTM D1102	Fraction of ash in bio mass plays a vital role in bio oil yield. Because high ash contains leads to decrement of bio oil and increase bio char and gas production.	0-20	(Guedes et al. 2017; Dhyani et al. 2018, Lim etal. 2016, Reddy et al. 2018; Lehto et al. 2013)
5	Carbon, Hydrogen	ASTM D-3178	Carbon is basic element of organic chemistry. Its proportion is directly connected to value of HHV. Hydrogen plays an important role in all fuel combustion systems. The greater the H + C/O ratio of a fuel, the greater it's HHV.	0-55	(Dhyani et al. 2018; Lim etal. 2016; Lehto et al. 2013)
6	Nitrogen	ASTM D-3179	N content in biomass is very much important in Environmental Pollution point of view. As value of N in bio mass decide emission of NOx	No significant effect	(Dhyani et al. ,2018, Lim etal.,2016, Lehto et al. ,2013)
7	Oxygen and Sulphur	ASTM D-3177	O content is usually established as the difference between the sum of the percentages of C, H, N, S and that of the ash. During combustion, the S in biomass fuels forms gaseous SO2, sometimes SO3, and alkalis. However, biomass is usually poor in S.	0-70	(Dhyani et al. 2018; Lim etal.2016, Lehto et al. 2013)
8	Heating Value	ASTM D-121	Calorific value refers to the heat produced by combustion of a unit quantity of feedstock in a bomb calorimeter with oxygen under a specified set of conditions.	5-20	(Dhyani et al. 2018; Lim etal. 2016; Lehto et al. 2013)
9	Fibre analysis	-	Bio mass with higher cellulose and hemi cellulose produce more bio oil compare to bio mass with high lignin because lignin decomposition is very difficult and it leads to production of bio char	Lignin (10-30%) Cellulose (30–50%), Hemi Cellulose (15–35%)	(Akhtar et al. 2012)
10	Thermal Analysis	-	Along with elemental analysis of bio mass knowledge of decomposition behavior is also important for pyrolysis process design. The commonly technique used for decomposition of bio mass are thermo gravimetric (TGA) and differential scanning calorimetric. In Thermo Gravimetric analysis (TGA) weight loss of bio mass is measured with increasing temperature.	-	(Dhyani et al. 2018)

TABLE 5. Feed-stock analysis of selected agro residues

	Fiber Analysis			Proximate Analysis				Ultimate Analysis					
	Cellulose %	Hemi cellulose %	Lignin %	Moisture %	Volatile Matter%	Fixed Carbon%	Ash %	C %	H %	N %	O %	HHV MJ/Kg	References
Sugarcane Bagasse	33-48	19-43	6-32	8.5	84.00	1.64	5.86	45.04	5.78	1.75	47.43	18.17	(Dhyani et al. 2018)
Corn cob	40.3-45	28.7-35	15-16.6	6.4	76.7	15.7	1.2	52.7	6.4	0.3	40.6	19.74	(Dhyani et al. 2018)
Wheat Straw	27.3-30	27.3-50	15-16.4	12.81	83.08	10.29	6.63	38.34	5.47	0.60	0.37	14.68	(Dhyani et al. ,2018)
Rice Straw	37	22.5	13.6	11.69	78.07	6.93	15.00	36.07	5.20	0.64	0.26	14.87	(Dhyani et al. 2018)
Rice Husk	31.3	24.3	14.3	10.89	73.41	11.44	15.14	41.92	6.34	1.85	0.47	12.87	(Dhyani et al. 2018)
Maize Stalk	28.78	23.27	22.23%	5.70	76.15	12.45	5.70	49.27	6.55	1.56	42.62	---	(Itani et al. 2018)
Cotton Stalk	40.69	6.69	12.37	7.37	70.11	17.84	4.68	48.89	5.21	1.19	44.71	15.96	(Chen et al. 2018)

EFFECTS OF CONVERSION PARAMETERS ON PRODUCTION OF BIO-OIL, BIO-CHAR, AND PYRO-GAS

Biomass conversion efficiency, also known as process yield, of pyrolysis process depends on various process parameters like temperature, Residence time, heating rate, feed rate, particle size, reactor type, gas flow rate etc. However, the most significant parameters are temperature, heating rate and residence time (Dhyani et al. 2018). Table 8 shows pyrolysis process yield in various parametric conditions of selected feedstock.

TABLE 6. Parametric value of different agro residue

Sr. No.	Name of agro Residue	Type of Pyrolysis	Temperature °C	Heating Rate (°C/min)	Resistance Time (Min.)	Bio char % Yield	Gas %Yield	Bio-oil % Yield	Reference
1	Sugarcane Bagasse	Slow Pyrolysis	380	45	60.	33.67	26.43	27.11	(Al arni et al. 2018)
			480	45-50	60	37.64	25.10	26.11	
			580	45-50	60	33.3	30.50	24.13	
			680	45-50	60	27.67	35.67	21.67	
2	Sugarcane Bagasse	Fast Pyrolysis	380	120-127	20	28.33	11.33	47.13	Al arni et al. 2018)
			480	120-127	20	25.34	14.12	50.89	
			580	120-127	20	29.86	15.46	42.81	
			680	120-127	20	29.53	17.94	39.77	
3	Corn cob	Slow pyrolysis	300	7	60	30	30	15	(Ates et al. 2009, Dhyani et al. 2018)
			400	7	60	30	30	16	
			500	7	60.	27	31	22	
			600	7	60	26	32	23	
			700	7		25	36	16	
			800	7		24	39	15	
4	Wheat straw	Slow Pyrolysis	300	20	60	36.1	31.4	32.5	(Demirbas et al. 2010; Dhyani et al. 2018)
			350	20	60	34.6	29.4	36.0	
			400	20	60	34.4	28.9	36.7	
			450	20	60	32.4	38.4	29.2	
5	Rice Straw	Slow Pyrolysis	300	20	60	35.1	39.0	25.9	(Demirbas et al. 2010; Dhyani et al. 2018)
			350	20	60.	35.0	37.9	27.1	
			400	20	60	33.5	38.1	28.4	
			450	20	60	33.1	39.8	27.1	
6	Rice Husk	Slow Pyrolysis	300	20	60.	43.3	20.8	35.9	(Demirbas et al. 2010; Dhyani et al. 2018)
			350	20	60	37.2	26.6	36.2	
			400	20	60	35.3	27.2	37.5	
			450	20	60	35.0	26.9	38.1	
7	Maize stalk	Fast pyrolysis	200	10	5	97	0	5	(Fu p. et al. 2010, Dhyani et al. 2018)
			300	10	5	80	3	18	
			400	10	5	31	16	52.5	
			500	10	5	25	18	53	
			600	10	5	22	20	53	
			700	10	5.	21	21	53.5	
			800	10	5	22	22	54	
8	Cotton Stalk	Slow Pyrolysis	400	7	NR	30.30	26.59	20.28	(Puttun et al. 2005; Dhyani et al. 2018)
			500	7	NR	29.17	26.51	22.38	
			550	7	NR	27.93	27.02	23.02	
			700	7	NR	25.56	32.02	18.59	

EFFECT OF TEMPERATURE

The function of reaction temperature is to provide heat energy required for decomposition of biomass bonds. In general, decomposition efficiency of biomass increases with increasing temperature. Table 6 shows temperature and corresponding % yield of bio-oil, bio-char, and pyro-gas. It can be seen from the table that in case of slow pyrolysis of sugarcane bagasse, with increase in reaction temperature, yield of bio-oil and gas decreases, while yield of bio-char increases. However, in case of fast pyrolysis of sugarcane bagasse, bio-oil yield increases up-to moderate temperature and then it decreases at high temperature, while yield of bio-char and bio-oil increases with increase in reaction temperature (Al arni et al. 2018). During slow pyrolysis of corn cob, yield of bio-oil and pyro-gas increases up-to moderate temperature, while yield of bio-char decreases but at high temperature reverse trend was observed for bio-oil, bio-char and pyro-gas (Ates et al. 2009; Dhyani et al. 2018). During slow pyrolysis of wheat straw, yield of bio-oil increases up to moderate temperature while yield of bio-char and pyro-gas decreases but at high temperature bio-oil and bio char yield decrease and yield of pyro-gas starts to increase. Similarly, for rice straw and rice husk, the yield of bio-oil and pyro-gas increases with increase in temperature while biochar decreases (Demirdas et al. 2010; Dhyani et al. 2018). In fast pyrolysis of maize stalk bio-oil and pyro-gas yield increase with increase in reaction temperature while yield of bio-char decreases (Fu p. et al. 2010; Dhyani et al. 2018). During slow pyrolysis of cotton stalks bio-oil yield and pyro-gas yield increase gradually while yield of bio char start decreasing but at high temperature bio-oil yield and bio char yield starts decreasing while pyro-gas continuously increases (Putun et al. 2005).

EFFECT OF HEATING RATE

Heating rate is an important parameter for biomass decomposition due to its effects on oil composition and hence quality of oil**.** Low heating rate in case of slow pyrolysis of corn cob at 7°C/min. % yield of bio-oil is less than pyro-gas and bio-char (Ates et al. 2009; Dhyani et al. 2018). For the same heating rate during slow pyrolysis of cotton stalks, the proportion of % yield of Bio-char >Pyro-Gas> Bio-oil (Puttun et al. 2005; Dhyani et al. 2005). For moderate heating rate of rice straw, wheat husk, maize stalk (10°-20°c/min), % yield of bio-oil > bio-char >pyro-gas (Fu p. et al. 2010, demirbas et al. ,2010, Dhyani et al. 2018). While for the same heating rate of rice straw pyro-gas> bio-char > bio-oil. During fast pyrolysis of sugarcane bagasse with very high heating rate bio-oil >pyro-gas> bio-char (Demirbas et al. 2010; Dhyani et al. 2018).

EFFECT OF RESIDENCE TIME

Residence time is the time that biomass sustains in a decomposition reactor at specific temperature to complete the reaction process. Low residence time up to 20 minute results in higher bio-oil yield compared to bio-char and pyro-gas for maize stalk and sugarcane bagasse (Al arni et al. ; Fu p. et al. 2010; Dhyani et al. 2018). Higher residence time of 60 minute, produces lower bio-oil yield compared to bio-char and pyro-gas for corn cob, sugarcane bagasse and rice straw (Demirbas et al. 2010; Al arni et al. 2018; Dhyani et al. 2018; Ates et al. 2009). However, the same residence time is 60 min. results into higher oil yield compared to bio-char and pyro-gas for rice husk and wheat straw (Dhyani et al. 2018; Demirbas et al. 2010).

It can be observed that bio-oil yield is optimum at moderate temperature, higher heating rate, and low residence time. Other than this particle size of biomass, gas flow rate, pyrolysis reactor type, feed rate and biomass fibre analysis etc. are affecting parameters on bio-oil, bio-char and pyro-gas [17]. Table 7 shows parametric range for different pyrolysis processes.

TABLE 7. Parametric range for different pyrolysis processes (Shah et al. 2019)

Parameters	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature	550–950	850–1250	1050–1300
Heating rate	0.1–1	10–200	>1000
Particle size	5–50	<1	<0.2
Solid residence time	450–550	0.5–10	<0.5

ANALYSIS OF BIO-OIL

Bio-oil is produced by condensation of gaseous products generated due to decomposition of biomass and composed of fragments of cellulose, hemicelluloses and lignin (C.K.Pchoi et al. 1978). Due to presence of moisture in feedstock and moisture generated as part of reaction during storage of bio-oil, it consists of two distinct phases i.e. *organic and aqueous*, in its structure. Organic phase is used as fuel after upgradation, while aqueous phase, cannot be used (S. Zhang et al. 2005). Bio-oil characterization is carried out by various physico-chemical and chemical analysis.

PHYSICO-CHEMICAL ANALYSIS

Physio-chemical properties of crude bio-oil derived from the residues are quite different from the hydrocarbon fuel. Properties of crude bio-oil depend upon factors like moisture content of feedstock, pyrolysis process parameters, reactor type etc. Due to dissimilarities in properties, it is immiscible with hydrocarbon fuel. Hence it needs to be upgraded (Solantausta et al. 1993). to use as fuel. Physio-chemical properties of selected agro residues are shown in Table 8.

TABLE 8. Physio-chemical Composition of Selected agro Residue

Agro Residue	Moisture content (% wt)	Oxygen Content (% wt)	Viscosity cSt	Acidity (pH)	Ash Content (% wt)	HHV/LHV MJ/Kg	Density Kg/dm^3	References
Sugarcane Bagasse	NR	46.94	8.934	2.74	0.24	20.072	1.198	(Islam et al. 2005)
Wheat straw	47.4	62.63	17.2	3.45	NR	13.6	NR	(Jahirul et l. 2012)
Corn Cob	32.2	53.2	6.7	3	0.1	15.8	NR	(Azeez et al. 2010)
Rice Straw	27.33	45.96	17.63	3.15	0.07	18	1.1883	(Li et al. 2015)
Rice husk	NR	63.27	4.783	2.68	NR	13.69	1.082	(Yusup et al. 2016)
Maize Stalk	22.5	47.5	13.8	3.2	NR	19.6	1.220	(Zheng et al. 2008)
Cotton Stalk	24.4	49.4	12.5	3.3	NR	17.77	1.160	(Zheng et al. 2008)

NR-Not Reported by author.

Significance of important physio-chemical properties i.e. moisture content, oxygen content, viscosity, acidity and ash content on behavior of bio-oil need to be analyzed (Y. solantausta et al. 1993).

MOISTURE CONTENT

Presence of moisture in bio-oil is mainly due to presence of moisture in feedstock and dehydration during pyrolysis process. Due to Solubilizing of hydrophilic, bio-oil cannot be separated from water. Too much moisture content, lower the heating value and flame temperature of the oil. Moreover, it also helps to lower down viscosity and pH value. It is measured by Karl Fischer titrimetric by following ASTM E-203 method (Mohan et al. 2006; Oasmaa et al. 2005; Khan et al. 2009; Zhang et al. 2007). Permissible range of moisture content in bio-oil is 15-30 % wt. depending on the pyrolysis process and condensation process.

OXYGEN CONTENT

Presence of oxygen in bio-oil plays a major role in variation of its properties as compared to hydrocarbons. It reduces heating value and makes bio-oil immiscible with hydrocarbons. It is generally calculated by the difference of C, H, N and S. Apart from its adverse impacts, it reduces emission of CO_2 by controlling combustion characteristics (Czernik et al. 2004; Zhang et al. 2007; Jacobson et al. 2013).

VISCOSITY

Viscosity is generally in the range of 15 – 30 cSt. It decreases with increase in room temperature and changes with time during storage. Higher water content controls viscosity. Also, it can be controlled with solvent like methanol and ethanol (Mohan et al. 2006).

ACIDITY

Bio-oil acidity is in the range of 2–3. Reason for this high value of acidity is generation of carboxylic acid during decomposition of biomass. High acidity leads to corrosion during transportation fuel pipe lines or in storage tanks which is a big challenge in usage of bio-oil (Czernik et al. 2004). Carboxylic acids such as formic acid and acetic acid become enormously high at high temperatures which require enhancing bio-oil upgradation technique before it gets used as transportation fuel (Jacobson et al. 2013).

ASH CONTENT

Ash is noncombustible matter present in bio-oil measured by following ASTM D482 standard (Zhang et al. 2007). Its presence in bio-oil is responsible for metallic corrosion and erosion. It creates a detrimental effect when its value is more than 0.1% wt. Presence of Alkali compound, mainly Na, K and vanadium are responsible metallic corrosion (Jacobson et al. 2013).

CHEMICAL CHARACTERIZATION OF BIO-OIL

Chemical characterization is an approach to identify presence of chemical compounds in bio-oil. It is analyzed mainly by Gas chromatography-mass spectrometry (GC-MS), Fourier transform ion cyclotron resonance-mass spectrometry (FTICR-MS), and nuclear magnetic resonance (NMR) (Demirbas et al. 2004). Table 9 shows the major chemical compound presence in bio-oil with % range (Oasmaa et al. 1999).

TABLE 9. Major compound of chemical characterization (Baloch et al. 2018)

Main components	Area % *Range
Phenolics	6-65%
Esters	2-44%
Aromatics and hetrocyclics	6-35%
Aldehydes	0-18%
Carboxylic acids	2-40%
Ketones	0-38%
Alkanes	9-13%
Nitrogenates	12-23%

Physio-chemical properties and chemical characterization of bio-oil show that bio-oil is a mixture of a variety of compounds, making it immiscible with hydrocarbon oil. It severely affects its combustion behavior, and significantly affects engine performance when used as fuel. So bio-oil upgradation is required before it is used as engine fuel.

UPGRADATION METHODS FOR BIO-OIL

High oxygenated compounds present in bio-oil makes it thermally unstable during storage and increases its acidity. High acidity produces detrimental effects during its usage. Hence, bio-oil cannot be directly used in raw form. Thermal stability can be controlled through various upgradation processes by reducing water and oxygen compounds (Jacobson et al. 2013). But enhancement of combustion behavior by reducing corrosion rate and improvement of H/C rate are the main challenge for researchers because the upgradation process of bio-oil is quite different compared to traditional crude oil (Zhang et al. 2005; Yang et al. 2015; Lian et al. 2016). Following are important bio-oil upgradation techniques.

EMULSIFICATION

Emulsification is the process of forming homogeneously mixed emulsions using surfactants. As compared to other techniques, emulsification is the simplest method to control the calorific value, cetane value, thermal stability and viscosity of bio-oil (Lin et al. 2016). Bio-oil is normally immiscible with hydrocarbon oil, but it can be emulsified by using surfactants. Some of the surfactants used for bio-oil emulsification are Span 20, Span 80 and Span 100, Span 85, Tween 85, Span 60, etc. (Solantausta et al. 1993).

CATALYTIC ESTERIFICATION

In Catalytic esterification, organic acid is converted into esters because presence of organic acid in bio-oil develops corrosion during transportation and storage. It is carried out by catalytic reaction of bio-oil with alcohol. Presence of a large number of aldehydes in bio-oil is the key challenge for bio-oil esterification (Lin et al. 2016).

CATALYTIC HYDROGENATION

In this method, pressurized hydrogen is passed to remove oxygenated compounds, Acidic compounds and Aldehydes to improve stability and combustion performance (Lin et al. 2016).

STEAM REFORMING

Formation of hydrogen and synthesis gas by passing steam through bio-oil is the fundamental principle of steam reforming. This gas can be used in the chemical industry (Lin et al. 2016). Nowadays, this method is studied by many researchers.

CATALYTIC CRACKING

Bio-oil catalytic cracking is the process to convert hydrocarbon fraction of bio-oil into hydrocarbon fuel with CO_2, CO, H_2O by using a catalyst. Mostly Zeolite catalysts (HZSM-5 etc.) used for this process because of its strong viability for reduction of oxygen compound, water, viscosity and acidity (Lin et al. 2016).

Many authors have put their effort for bio-oil upgradation through different methods. Catalytic cracking, Catalytic hydrogenation and Steam reforming are the advanced techniques but requirement of gas for this technique create GHG emission. While emulsification is the cheapest method for generation of bio-oil-diesel blend through emulsifiers / surfactants.

ANALYSIS OF BIO-CHAR

Bio-char is the solid residue generated during the pyrolysis process along with bio-oil and pyro-gas. It can be used as a direct or blended form for soil improvement and protection against particular environmental pollution etc.

TABLE 10. Available nutrient from different agro residue

Agro waste	C%	N%	P%	K%	S%	Ca%	Mg%	Fe%	Cu%	References
Sugarcane Bagasse	78.6	0.87	0.67	2.23	---	7.33	1.77	0.43	---	(Y.Solantausta et el.,1993, Kameyama et al. ,2012, Yao et al. ,2012)
Wheat straw	60.8	1.41	---	1.26	---	12.6	9.88	1.94	---	(Bruun et al. 2012; Cheng et al. 2012; Kloss et al. 2012, Solaiman et al. 2012; Sun et al. 2012; Yoo et al. 2012 , Zheng et al. 2012)
Corn Cob	58.8	1.06	2.35	19.0	0.37	8.64	7.10	7.30	115	(Brewer et al. 2012, Rajkovich et al. 2012; Feng et al. 2012; FReddo et al. 2012, Hale et al. 2012; Jia et al. 2012; Kammann et al,2012, Kineey et al. 2012; Nelissen et al. 2012; Rajkovich et al. 2012)
Rice Straw	43.6	1.40	1.20	0.70	3.90	---	---	---	---	(Lu et al. 2012; Mekuria et al. 2012; Wang et al. 2012)
Rice husk	43.6	1.40	1.20	0.70	3.90	---	---	---	---	(Lu et al. 2012; Mekuria et al. 2012; Wang et al. ,2012)
Maize Stalk	21.54	2.06	0.84	4.25	--	--	--	--	--	(Sherene et al.)
Cotton Stalk	76.2	0.67	0.39	1.11	--	---	---	---	---	(Sherene et al.)

TABLE 11. Nutrient retention from different agro residue

	pH	Surface area($m^2\ g^{-1}$)	CEC(mmolc kg^{-1})	References
Sugarcane Bagasse	7.59	113.6	115	(Kameyama et al. 2012)
Wheat straw	8.80	26.65	103	(Bruun et al. 2012)
Corn Cob	9.27	107.2	607	(Brewer et al. 2012)
Rice Straw	9.17	42.15	212	(Lu et al. 2012)
Rice husk	9.17	42.15	212	(Lu et al. 2012)
Maize Stalk	9.9	1.5	45	(Sherene et al.)
Cotton Stalk	10.6	0.9	39	(Sherene et al.)

Table 10 and 11 shows average of total nutrient value available in bio-char from different agro residues. Presence of N in bio-char shows a good carrier for the growth of soil bacteria, while P present in bio-char helps to improve enzyme efficiency and soil pH. Presence of S in bio-char enhances oxidation and reduction capacity of soil. It is observed that the incremental effect of pH leads to detrimental effects on surface area and Cation exchange capacity (CEC). However, bio-char is greatly affected by pyrolysis temperature and particle size distribution.

Thus, retention of bio-char to the soil replaces the nitrogen, carbon and other important plant nutrients that vanish due to frequent harvesting of crops and improves soil fertility.

ANALYSIS OF PYRO-GAS

Pyro-gas is the gasses that are produced during the pyrolysis process. It comprises carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), ethane or ethylene (C_2H_4), propane or propylene (C_3H_6). Since this gas comprises a substantial amount of carbon dioxide in it, it can be used as fuel (Goyal et al. ,2008). Most effective use of this gas is as carrier gas during the pyrolysis process as this gas contains a considerable amount of heating value (Bridgewater et al. 1994). Yang Yu et al found HHV of corn stalk 13 MJ/m^3 while the same for rice husk was 15 MJ/m^3. Author also found that the HHV value of pro-gas increases sharply with the increase in temperature (Yu y. et al. 2016).

ECONOMICAL ASSESSMENT OF BIOFUEL PRODUCTION

Apart from Technological aspects, economics of bio- fuel production is of paramount importance for commercial level acceptability of the biofuels. Economics of biofuel production is affected by many external parameters like market fluctuation, weather conditions that affect logistic and agricultural operation and subsidy government policy etc. Despite these external parameters, the area of biofuel still needs to be explored technologically as well as economically. Techno Economic analysis (TEA) is the method used by researchers for economic evaluation of biofuel production.

GENERAL METHODOLOGY OF ECONOMIC EVALUATION

Biofuel production cost varies with production process, production capacity, geographical pathway and government subsidy policy etc. Biomass production pathway varies with first to third generation biomass. The economic evaluation is based on some common techno economic indicators i.e. payback period, net present value, fixed capital cost, total manufacturing cost, rate of return and break-even price etc. (Kou et al. 2011). Table 12 shows Techno Economic analysis of bio fuel derived through various techniques from first generation to third generation sources. Operating cost for different processes for different agro waste listed in Table 16 directly implied that operating cost for biodiesel and gasification process is little beat less but it cannot accommodate agro waste as feedstock while pyrolysis process can accommodate agro waste that may directly reflect on total manufacturing cost.

TABLE 12. Economic Evaluation of biofuel based on feedstock and Technology

Sr. No	Feed stock and process	Process	Operating cost ($/lit)	References
1	Soya bean	Biodiesel	1.08	(Hung et al. 2016)
2	Sugarcane	Ethanol	0.48	(Hung et al. 2016)
3	Forest residues	Pyrolysis	1.65	(Carrasco et al. 2017)
4	Corn Stover	Fast pyrolysis and Gasification	1.48	(Li et al. 2015)
5	Energy crop	Fast Pyrolysis	1.56	(Sarkar et al. 2010)
6	Gasoline	---	1.3	(Trippe et al. 2013)
7	Lignocelluloses biomass	Ethanol	0.36	(He et al. 2011)
8	Algae	Hydrothermal Liquefaction	0.679	(Ou et al. 2015)
9	Corn Stover	Fast pyrolysis	0.82	(Wright et al. 2010)
10	Waste cooking oil	Biodiesel	1.298	(Mohammadshirazi et al. 2014)

LIFE CYCLE ASSESSMENT ANALYSIS

Life cycle assessment (LCA) is the tool to assess impact of end product throughout the life. The conversion of lignocellulosic biomass to useful end product carried out in 3 phases: 1) Biomass pre and post harvesting and transportation. 2) biomass site operation and its up gradation. 3) Flattening and reprocessing of plants. LCA is carried out by different software i.e. GREET [Greenhouse gasses, Regulated Emissions, and Energy use in Transportation], SigmaPro, GHGenius, TEAM [Tools for Environmental Analysis and Management] etc. (Roger et al. 2012; Mann et al. 2001). Eco Indicator 95/99 and CML (developed by Institute of Environmental Science of Leiden University) are used to analyze the environmental impacts of different feedstock (Robert et al. 2010; Faix et al. 2010).

DIFFERENT PHASES INVOLVED IN A SYSTEM BOUNDARY FRAMEWORK

The LCA of thermo chemical conversion process is carried out in 3 phases as discussed earlier. Figure3 shows required input and output during each phase. Phase 1 includes two processes: biomass cultivation and transportation. Important measuring indicators for this phase are usage of land, carbon adoption, use of fertilizer and pesticides, impact on soil after removal of agro residue and transportation distance from site to biomass storage (Koroneos et al. 2008). The removal of agro waste is a key factor because it affects the environment and creates adverse impact on soil. If sufficient straw is not left in the field it reduces soil organic matter, nutrients from the soil and yield of biomass forever. That's why straw management is required to balance the entire soil ecosystem needed to include in LCA (Gabrielle et al. 2008).

Phase 2 of LCA is for biomass pretreatment processes like crushing, chopping, grinding and drying etc., This phase varies with process to process. Therefore, different conversion technologies are having variation in environmental impact.

Phase 3 of LCA is for reprocessing and flattening of plants. This phase involves: 1) Flattening of plant 2) Extraction, Transportation and reprocessing of plant equipment 3) Dealing with Non-Recyclable material.

REVIEW OF LCA STUDIES ON THERMO -CHEMICAL PROCESSING OF BIOMASS

LCA of different thermo chemical conversion processes is shown in table 13. This study needs to consider Global warming potential (GWP), Net energy ratio (NER), greenhouse gasses (GHGs) etc. By referring various literature of different process for LCA i.e. combustion, gasification, liquefaction and pyrolysis, it can be concluded that transportation of biomass, fuel consumption during site process, bio-oil yield, and electric power consumption also play vital roles in determining the GHG footprint. GHG emission through pyrolysis process is comparatively less than fossil fuel like gasoline and diesel particularly

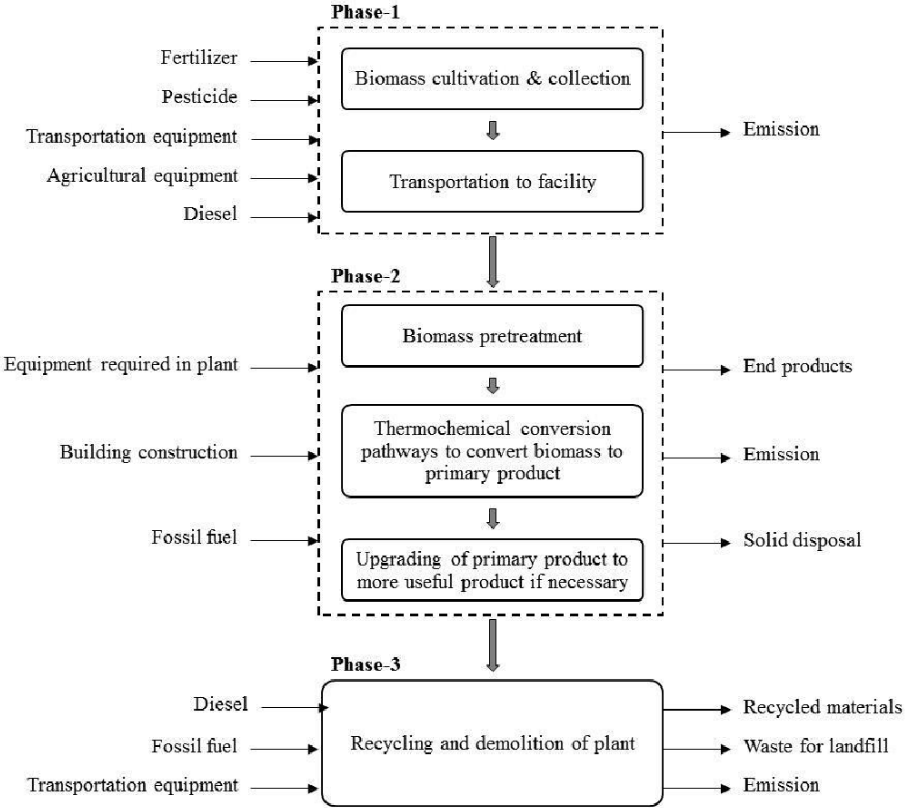

FIGURE 3. generalized system boundary for an LCA analysis

TABLE 13. LCA of different conversion process

Biomass conversion Technology	Feed stock	LCA and Environmental Impact	Reference
Combustion	Rice Husk	CO_2 emission from rice husk derived electricity is 217g/KWh which is too high as compare to other crop residue.	(Shafie et al. 2012)
Combustion	Forest Residue	The GHG emissions depends on moisture content.	(Thakur et 9al. 2014)
Gasification	-----	GHG emissions can be significantly reduced (from 68 to 17 Gg CO_2-eq/PJ) by increased utilization of residual biomass. CO_2 emissions lower from (35-178 g-CO_2/kWh) than coal fired systems (975.3 g-CO_2/kWh)	(Farzad et al. 2016)
Gasification	---	Gasification of forest residue reduce 80% GHGs compare to natural gas	(Thornley et al. 2015)
Liquefaction	Palm	Biomass pretreatment during palm liquefaction process contributes 99.78% of the GWP, with 98.49% of CO_2 emission.	(Chan et al. 2015)
Liquefaction	Algae	HTL-derived algae fuels were found to have lower greenhouse gas (GHG) emissions than petroleum fuels.	(Liu et al. 2013)
Pyrolysis	Forest Residue	Pyrolysis of forest residue are estimated to emit fewer greenhouse gases than conventional gasoline	(Iribarren et al. 2012)

CHALLENGES

Despite the many advantages of the pyrolysis process using agro residues as feedstock material, it is not yet commercialized due to following challenges:

1. Bio-oil is chemically and biologically complex oil due to large no. of constituting chemical compounds, which makes it difficult to process to get derided properties of an efficient fuel. So, suitable oil processing technologies and methodologies are to be developed to ensure uniformity in composition and quality of oil.
2. Depending upon the feedstock sources, the values of the bio-oil fuel properties are much wider than the properties of hydrocarbon fuel. It offers a great challenge to optimize the oil extraction and upgradation processes.
3. Bio-oils are thermally and chemically unstable due to susceptibility to change viscosity with temperature and time. It is suggested to either filter out the viscosity affecting constituents or neutralize the effects of it by suitable treatments.

RECOMMENDATIONS FOR FUTURE RESEARCH

From the reviewed literature, it has been found that research has been carried out on performance of agro residue-based bio-oils as engine fuel. However, very limited works have been reported on the production of stabilized oils and its performance analysis as engine fuel. Some potential areas have been identified for the future research as briefed below.

1. *Production of stabilized oil from different agro residues*: Proper extraction of crude oil contents from agro residues and proper procedure to upgrade it into stabilized oil need to be explored and developed for high oil containing biomasses separately.
2. *Mixing/Blending methodology for agro residue-based bio-oil:* Due to different chemical and biological structures of agro residues, proper mixing methods and Blending ratios are required to be developed to ensure desired miscibility and long-term stability.
3. *Performance and emission analyses*: Performance and emissions analyses are to be evaluated to assess the feasibility of stabilized and blended agro residues-based biodiesel as engine fuel.
4. *Life cycle Analysis (LCA) of agro residue-based Biodiesel*: Detailed investigations on LCA for agro residue-based Bio-oil needs to be evaluated and its comparison with different biodiesel is required.

CONCLUSION

Due to abundant availability of non-edible agro based residues after post-harvest practices, and favorable constituting elemental analysis of residues suggest the potential of sustainable sources of high value-added bio energy products like bio-oil, bio-char and pyro-gas. Pyrolysis is found to be one of the most suitable methods for conversion of residue biomass into value added products.

Properties of raw bio-oils derived from agro residues are dissimilar to hydrocarbon oil due to its chemical structure. raw bio-oils are to be upgraded in order to improve its stability, anti-corrosiveness, and miscibility with hydrocarbon fuel. Amongst various bio-oil upgradation techniques, emulsification is found to be the most economical and efficient method. Bio-char analysis of selected feedstock shows that soil nutrition retention can be possible with investment of biochar in soil. Pyro-gas analysis shows that non condensable gas produced after the pyrolysis process can be used as fuel for feedstock heating.

Techno Economic analysis of the bio-oil production shows that bio-oil extraction through the pyrolysis process is an economical process as compare to the other conversion processes. LCA of bio fuel through different conversion processes have been reviewed for GHG emission, global warming potential, net present value etc. which shows pyrolysis process has potential to reduce GHG emission.

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DECLARATION OF COMPETING INTEREST

None

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