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A Review On Physicochemical Characterization And Pyrolysis Kinetics Of Biomass And Plastic

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ABSTRACT

Rapid depletion of petroleum resources and enhancement in energy demand have motivated the researchers to discover alternate path to generate sustainable source of energy like biooil that could replace convectional fossil fuel. Lignocellulosic biomass and plastics are attractive for energy conversion because of their low cost and bulk availability. The co-pyrolysis of biomass and plastic can significantly improve the quantity and quality of pyrolysis oil. It is one of the most widely used techniques for thermo-chemical conversion of biomass and plastic waste, which can minimize pollution problems and regain beneficial energy, into oil. The physicochemical characteristics of plastic and biomass suggest its potential for co-pyrolysis, whereas, solid state thermal decomposition kinetics provide valuable information for designing and operating industrial biomass and plastic conversion systems. This review paper presents valuable information about the physiochemical characteristics of various lignocellulose biomass and plastic, different kinetic models, and mathematical approximations to calculate kinetics parameters. Thermogravimetric analysis (TGA) is used to obtain the thermal degradation of biomass and kinetic parameters of pyrolysis process. TGA data applied to iso-conversional model-free and model-fitting techniques to determine kinetic variables such as pre-exponential factor, activation energy and reaction order of pyrolsis process.

Keywords: Biomass, Plastic waste, Pyrolysis, Physicochemical characteristics, Thermogravimetric, Kinetics.

1. Introduction

Development of any country depends on the availability of conventional fuel sources mainly fossil fuel. Due to the rapid development this fossil fuel are decreasing accordingly. The increasing trend of oil prices in current years and the environmental issues associated from combustion of such fuels are motivate to shift over the alternative sustainable renewable energy sources. Biomass is a significant renewable and sustainable source of energy in this context. Biomass refers to organic carbonaceous materials, such as crop residues, wood products, dried vegetation etc. It is the best sustainable power source that can be transformed into certain fuels like bio- oil as liquid, char as solid, and gas. In recent years, Biomass would be assessed to contribute 15-50% of world's essential energy utilization constantly in the year of 2050 (Demirbas, 2004; Uzoejinwa et al., 2018). Biomass with lower amount of nitrogen, sulfur and ash is preferred to produce bio oil due the less generation of environment contaminants. Moreover as the biomass utilizes the waste thus reduce the garbage load (A. Kumar and Prasenjit, 2016).

Plastics have been fundamental material and their applications in different fields are deliberately growing. Plastic manufacturing and its utilization is expanding every day at disturbing rates with the growth of human population, quick financial development, urbanization and change in the way of life. The worldwide plastic creation was assessed around 300 million tons each year and its constantly expanding each year (Kumar Jha & Kannan, 2020). As the plastic hasnon-degradable in nature thus exist in environment for longer time subsequently creates environmental issues. These days plastic waste can be utilize in three different ways: dumping, burning and reusing. The biggest quantity of plastic wastes is discarded via landfilling, incineration and reusing are 65-70%, 20-25% and 10%, respectively (Miskolczi et al., 2004). Landfilling or burning of plastic waste is not the proper disposal method, due to the fact the landfilling has the threat of filtering and soil impregnation. Whereas, burning produces numerous pollutions such as NOx, SOx, which adversely affect the climate (Pinto et al., 1999). The major path adopted to turn organic materials into a value added product is convert biomass into various bio-fuels through gasification, pyrolysis and liquefaction (Sharma et al., 2015). Pyrolysis is efficient waste to energy conversion methods which produce solids, liquids and gases product in which liquid (oil) can be used as fuel in industry. It performed under the inert atmosphere (Collard & Blin, 2014).

1.1 Source of biomass

Biomass fuels consist of wooden, short-pivot woody yields, agricultural wastes, short-revolution herbaceous species, wood squanders, bagasses, mechanical deposits, waste paper, municipal stable waste, sawdust, bio-solids, grass, waste

from food handling, sea-going flora and green growth creature wastes, and a large group of different materials. Biomass can be a best substitute of natural oil which is inexhaustible (Demirbas, 2004; Zhang et al., 2010).

1.2 Source of Plastic

Expanding population has expanded the interest of plastic because it is a tough, versatile, and low cost origin. Industrial packaging and municipal solid waste are the major source of plastics waste. Municipal solid waste consist of plastic waste from residence-holds and farming waste that involves food coverings, poly bags, dairy products, squeeze bins, pouch, compost packs, lines, fittings, nets and cross section etc. The Industrial plastic waste is created principally by destruction organizations, charged gear's, and vehicle production etc (Singh & Ruj, 2015).

2. Lignocellulosic biomass

Biomass consists of a wide variety of natural materials that are typically made out of cellulose, hemicellulose, lignin, lipids, proteins, easy sugars and starches. Among these mixtures, cellulose, hemicellulose, and lignin are the three fundamental constituents (Zhang et al., 2010). During thermal degradation of biomass, hemicellulose degradation occurs in the lower temperature range of 220-315°C, however, cellulose degradation occurs in the higher temperature range of 315-400°C. Although, lignin degradation occurs gradually from ambient temperature to 900°C (Dhyani & Bhaskar, 2017).

2.1 Cellulose

Cellulose is a linear and long chain glucose polymer. In cellulose, large part consists of linear chains of glucopyranose units. It is highly stable and strength polymer chain which has capability against resistant to chemical attack (Dhyani & Bhaskar, 2017; Mckendry, 2002a). The level of polymerization of cellulose is higher than that of hemicellulose which is fifty to two hundred monomers (Dhyani & Bhaskar, 2017).

2.2 Hemicellulose

Hemicellulose is a combination of heterogeneous branched polysaccharides which is predominantly made from various sugars like mannose, glucose, xylose, methylglucuronic, arabinose and galaturonic acids. Its mean atomic weight is less than thirty thousand (Mckendry, 2002a).

2.3 Lignin

Lignin can be observed collectively of no particular shape, high atomic weight, synthetically similar blends. Structure of lignin are mainly includes phenyl-propane (Dhyani & Bhaskar, 2017). Lignin percentage might differ from 23 to 33 % in softwoods 20 to 35 %, in hardwoods and 16 to 40% in the organic materials. It is present in vacant area surrounding of cellulose micro fibrils covered by hemicellulose. Lignin assumes a limiting part among cellulose and hemicellulose inside the cell wall (Mckendry, 2002).

Table 1. Lignocellulosic configuration of various biomass.

Biomass	Cellulose(%)	Hemicellulose(%)	Lignin(%)	References
Pine needle	34.5	29.1	31.7	(A. Kumar & Prasenjit, 2016)
Banana waste	13.2	14.8	14	(Dhyani & Bhaskar, 2017)
Rice Husks	40.20	27.30	18.10	(Qing-lan et al., 2015)
Corn cob	39.30	28.70	19.60	(Li et al., 2014)
Bamboo Sawdust	23.59	44.12	24.49	(Pepelyshev & Tsogtsaikhan, 2015)
Wheat Straw	33-40	20-25	15-20	(Mckendry, 2002a)
Switch grass	30-50	10-40	5-20	
Birch	56.47	24.79	12.17	(Shen et al., 2009)
Elephant grass	39.14	19.9	6.18	(Fontes, 2014)
Sugarcane Bagasses	47.6	39	11.2	(Varma & Mondal, 2016)
Timothy grass	31.5	24.0	27.5	(Naik et al., 2010b)
Flax straw	36.00	34.5	29.00	(Naik et al., 2010a)
Almond shell	30.5	35.00	32.00	(Caballero et al., 1997)
Coir pith	28.00	16.00	32.00	(Raveendran et al., 1995)
Subabul wood	40.00	25.00	25.00	
Coconut coir	41.3	25.9	17.8	
Shea tree sawdust	45.9	20.3	29.9	(Ayeni et al., 2015)
Castor beans cake	46.9	4.7	32.3	(Santos et al., 2013)
Tabacco waste	30.3	13.0	20.4	(Cardoso et al., 2011)
Sorghum bagasses	41.0	24.0	10.0	
Barley straw	48.6	29.7	27.7	(Sellin et al., 2016)
Maize stalk	29.7	15.2	17.2	(N. Ali et al., 2016)
Hazelnut shell	28.8	30.4	42.9	(Jahirul et al., 2012)

3. Biomass conversion technologies

Thermo- chemical and bio- chemical/organic are the process used for conversion of biomass into energy. Bio-chemical transformation envelops two method choices: absorption and maturation. Thermo chemical processing of biomass utilizes catalysts and heat to convert organic materials and polymers into clean energy as well as different beneficial chemicals. In comparison with biochemical methods, thermo chemical methods happen quicker (in no time flat to hours); though the previous requires time (in the scope of days) to finish (Dhyani& Bhaskar, 2017).

3.1 Thermo-chemical conversion

Thermo-chemical conversion is a method for breaking down the organic material into fuel by the action ofheat energy. The fuel obtained from the thermo chemical transformation of organic materials is liquid and gas in which the liquid is termed as bio-oil (Ryu et al., 2020). Inside thermo-chemical subtitute four interchange alternatives are available: ignition, pyrolysis, gasification and liquefaction (Mckendry, 2002a).Thermo chemical transformation procedures like pyrolysis and gasification can give an optimal pathway to convert biomass and plastic wastes into fuel (Burra & Gupta, 2018).

3.1.1 Pyrolysis process

Pyrolysis is a systematic thermo-chemical transformation method that plays essential part in organic materials change. (H. Yang, 2007). Pyrolysis is unique in relation to burning since it happens without air, hence no creation of unsafe emissions and the recuperation of the product is constantly accomplished (Oyedun et al., 2013). Depending upon the working conditions, the pyrolysis approaches may be categories into three subcategories: traditional pyrolysis (carbonization), flash Pyrolysis and fast Pyrolysis. Conventional pyrolysis is also called moderate or carbonization which works at low temperature and low heating rate 0.1-1 ºC/s. Fast pyrolsis requires low temperature, higher heating rate 10-200 ºC/s and short residence time to yield bio fuel as a product. Flash pyrolsis requires excessive high temperatures, with extremely short residence times, which gives a good stability among the yield and the synthesis of the oil (Vasile & Brebu, 2006).

4. Physicochemical properties of biomass

Physical, chemical and thermal attributes of biomass are essential to choose the biomass as a feed stock for conversion it into bio oil (A. Kumar & Prasenjit, 2016).

4.1 Proximate analysis

Proximate analysis describes the fundamental characteristics of biomass in terms of moisture (M), volatile matter (VM), aside from water fixed carbon (FC) which is the non-volatile part of biomass, and ash (A) which is mainly inorganic materials, remained unburned after combustion. Compared to biomass with high fixed carbon, the rate of conversion for biomass with excessive volatile matter is highest (Dhyani & Bhaskar, 2017).

4.2 Ultimate analysis

Ultimate analysis is vital for the selection of biomass for pyrolysis purpose. It gives the composition of carbon, hydrogen, nitrogen, sulfur and oxygen (CHSNO) of the feed stock. The composition of the components received from these analysis offer superior correlation among the feedstock (Dhyani & Bhaskar, 2017). **Table 2** shows the Proximate and ultimate evaluation of various biomasses with their heating value.

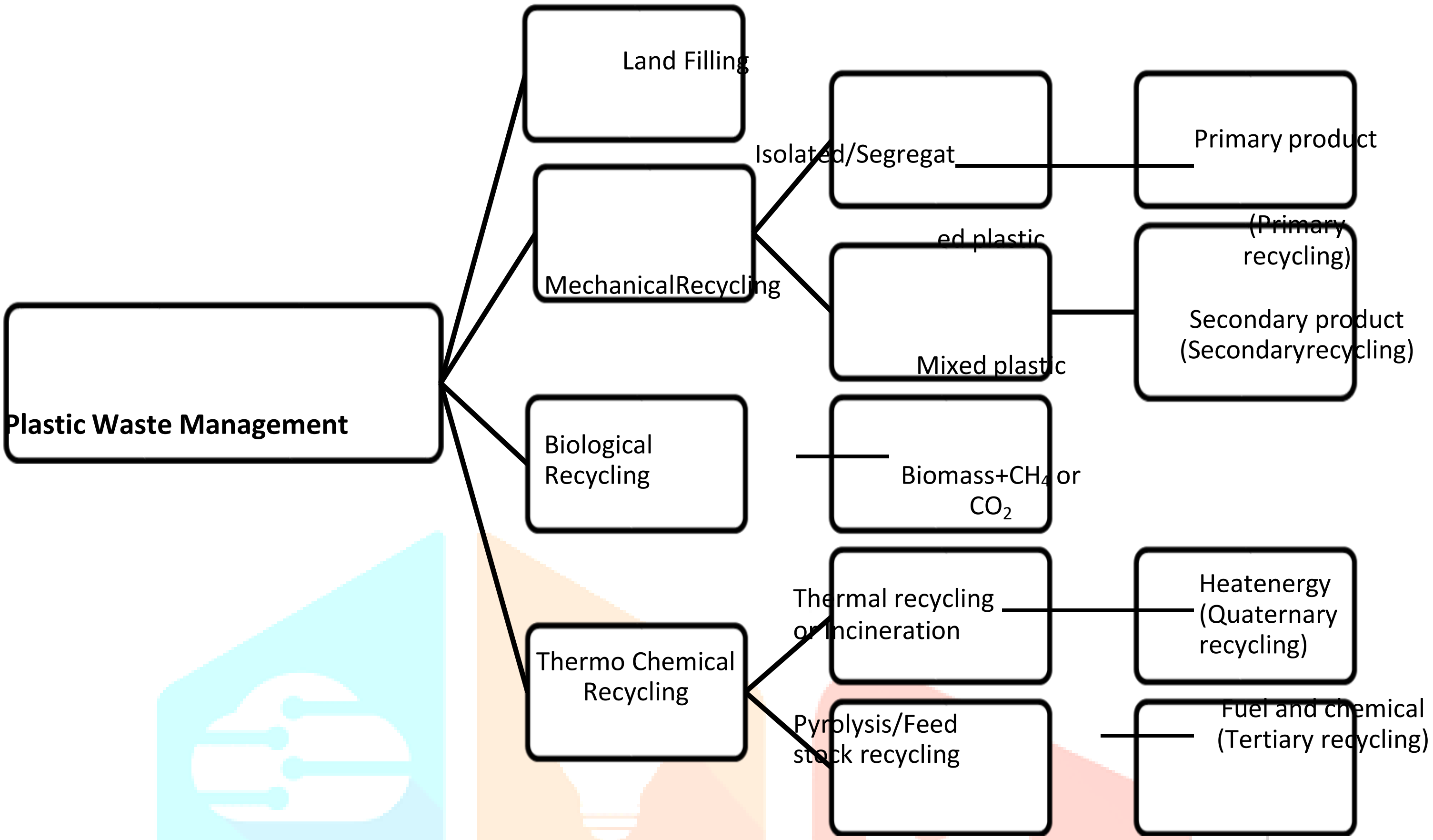
Table 2. Proximate and ultimate evaluation of various biomasses with their heating value.

Biomass	**Proximate analysis /wt. %**				**Ultimate analysis /wt. %**					**HHV (MJ/ Kg)**	**References**
	M	**VM**	**A**	**FC**	**C**	**H**	**N**	**O**	**S**		
Elephant grass	10.0	65	14.7	6.0	44.5	5.4	1.4	31.8	-	15.6	(Abbasi & Abbasi, 2010)
Vetiver grass	5.73	50.57	10.86	2.84	42.2	5.5	0.6	51.54	-	15.8	(L. Singh et al., 2017)
Para grass	7.23	79.45	9.32	_	44.73	46.8	0.98	_	0.24	15.04	(Ahmad et al., 2017)
Corn stover	8.5	76.7	6.1	8.2	41.9	6.5	0.6	44.8	0.2	15.9	(Carrier et al., 2013)
Maize stalk	1.14	62.94	4.20	30.24	40.72	5.68	0.92	47.01	0.12	15.87	(N. Ali et al., 2016)
Oak wood	_	80.6	1.0	18.5	49.3	6.2	0.1	44.5	0.0	18.19	(Alonso, 2016)
Walnut shell	6.98	76.45	0.58	15.9	47.5	6.71	0.21	45.5	-	17.83	(Özsin, 2017)
Beech wood	_	85.7	0.5	13.9	45.52	6.34	0.16	47.98	_	_	(Ding et al., 2016)
Tree root	-	79.19	6.64	14.1	43.2	5.32	1.67	49.5	0.24	-	(Meng et al., 2013)
Peanut shell	8.03	58.38	11.31	22.29	37.87	5.18	1.57	55.23	0.13	_	(Yuan et al., 2015)
Coffee husk	8.2	-	8.3	-	43.1	5.93	1.55	32.22	0.67	16.79	(Cruz et al., 2018)
Switch grass	_	82.58	2.86	14.56	48.81	6.32	0.53	41.58	0.08	19.42	(Agarwal & Lattimer, 2014)
Corn stover	_	82.13	5.01	12.86	53.27	5.67	0.62	35.33	0.10	19.76	
Olive residue	7.3	74.8	5.1	12.8	50.9	5.28	-	38.6	-	-	(Ounas et al., 2011)
Sugarcane bagasses	6.7	91.7	10.3	8.3	51.9	6.9	0.4	40.5	0.5	16.6	(Aboyade et al., 2013)
Sawdust	5.05	81.46	0.76	13.4	52.2	9.06	0.11	38.3	0.20	-	(Silva, n.d.)
Elephant grass	14	74	11	15	41.6	5.5	1.78	51.1	-	16.8	(Fernandes et al., 2013)
Shea meal	-	66.3	5.0	28.7	48.6	5.9	2.9	37.7	-	19.8	(Munir et al., 2009)
Pine	12.9	71.5	0.3	15.3	41.9	4.5	0.2	40.2	-	16.8	(Shen et al., 2009)
Oak	8.8	76.8	0.2	14.2	45.4	5.0	0.3	41.3	-	18.9	
Banana leaves	7.9	78.2	6.2	15.6	43.2	6.23	0.98	49.0	0.49	17.1	
Pine needle	-	74.2	1.7	24.1	45.8	5.4	1.0	46.1	-	18.5	

5. Various techniques of plastic waste management

Due to the increase in population of world, the use of plastic material has also increases. Low cost and easily availability of plastics make it a suitable substitute for the replacement of wooden and cloth items in our regular life. Their non digestive and non-environmental friendly nature create a several problems in their disposal. There are the numerous techniques (Fig 1) for disposal of plastic waste i.e. dumping, mechanical reprocess, organic recovering and thermo-chemical recycling (Panda et al., 2010).

Figure 1. Various ways for plastic waste management (Panda et al., 2010; R. K. Singh & Ruj, 2015).



6. Physicochemical properties of plastic

Physicochemical properties of plastics vary according to type of plastic. Volatile matter, moisture, ash content and fixed carbon are evaluated in proximate analysis. Generally the plastic can be a suitable feed stock due to its high volatile matters as compared to biomass, which decides the high yield of oil in pyrolysis operation. In view of **Table 3**, it becomesvisible that all plastics contain extremely high volatile matter and less ash. Heating value of plastics is also high as compared to biomass. **Table 3** summarized different types of plastic with their proximate and ultimate evaluation**.**

Table 3. Proximate and ultimate evaluation of various plastics with their heating value.

Types of plastic	Proximate evaluation /wt. %				Ultimate evaluation /wt. %					HHV(MJ /Kg)	References
	M	VM	A	FC	C	H	N	O	S		
Polyethylene terephthalate(PET)	0.00-0.46	88.61-91.75	0.00-0.02	7.77-11.39	62.7	44	0.0	32.8	0.0	23.0-30	(Abnisa & Wan Daud, 2014; Ali et al., 2016; Anuar Sharuddin et al., 2016; Uzoejinwa et al., 2018)
High-density polyethylene (HDPE)	0.00-0.61	86.83-99.81	0.00-0.18	0.01-13.17	85.5	14.5	0.0	0.0	0.0	49.0	(Abnisa & Wan Daud, 2014; Al-Salem et al., 2017; Anuar Sharuddin et al., 2016)
Polyvinyl Chloride(PVC)	0.00-0.80	93.70-98.57	0.00-1.40	0.03-6.30	38.0	5.0	0.0	0.0	0.0	21.2	(Abnisa & Wan Daud, 2014; Anuar Sharuddin et al., 2016; Uzoejinwa et al., 2018)
Low-density polyethylene(LDPE)	0.30-0.74	94.82-99.70	0.00-0.00	0.00-5.19	85.70	14.20	0.05	0.05	0.00	46.4	(Al-Salem et al., 2017; Anuar Sharuddin et al., 2016)
Polypropylene (PP)	0.00-0.15	95.08-99.60	0.00-1.99	0.40-3.55	97.9	8.3	0.0	0.0	0.0	46.0	(Al-Salem et al., 2017; Anuar Sharuddin et al., 2016; Uzoejinwa et al., 2018)
Polystyrene(PS)	0.18-0.25	97.85-99.63	0.00-1.99	0.12-0.16	97.9	8.3	0.0	0.0	0.0	41.0	(Al-Salem et al., 2017; Anuar Sharuddin et al., 2016; Uzoejinwa et al., 2018)
Polyethylene(PE)	0.10-0.30	98.87-99.50	0.00-0.99	0.04-0.20	86.0	14.0	0.0	0.0	0.0	40.5	(Anuar Sharuddin et al., 2016; Uzoejinwa et al., 2018)

7. Co-pyrolysis of biomass with plastic

Pyrolysis of biomass is not much effective for production of aromatic hydrocarbon because it contain less amount of hydrogen and excessive amount of oxygen. This might be conquer by co-pyrolysis of biomass along with plastic. Now days, co-pyrolytic strategies have gotten a lot of consideration since they give an alternative method of disposal andcan undoubtedly convert polyolefin's and cellulose determined materials into high worth feedstock. The particular advantages of this strategy possibly consists the decrease in volume of plastic waste; the recuperation of different chemicals, and the substitution of petroleum products (Chattopadhyay et al., 2008). **Table 4** represents the summary of co-pyrolysis of plastic and biomass.

Table 4. Co-pyrolysis of plastic mixed with biomass

Types of Plastic	**Biomass**	**Pyrolysisprocess parameters**	**References**
Plastic waste	Pine residue	Temperature at 400°C for30minutes ;1.0MP; stainless autoclavewith furnace	(Dorado et al., 2015; Uzoejinwa et al., 2018)
Polystyrene	Karanja seeds Niger seeds	Temperature at 550°C ;1.0MPa; stainless steelreactor	(Shadangi & Mohanty, 2015; Uzoejinwa et a2018)
Polypropylene	Cotton Straw	Temperature at 380-480°C;fixed bed reactor	(Hua et al., 2015; Uzoejinwa et al., 2018)
Low density polyethylene, Polypropylene, Polystyrene	Pine cone	Temperature at 500°C; 10°C/min underatmospheric pressure; glass reactor	(Brebu et al., 2010; Uzoejinwa et al., 2018)
Polypropylene	Wood chips	Temperature at 500°C; fixedbed reactor	(Jeon et al., 2011; Uzoejinwa et al., 2018)
Low density polyethylene	Sunflower stalk Cedarwood Fallopia Japonica stem	Temperature at 600°C; 10min; 100cm^3/min of argon flow; tubular reactor	(Uzoejinwa et al., 2018; J. Yang et al., 2016)
Polystyrene	Cellulose	Temperature at 500°C; 5°C/min; argon flow rate of 5dm^3/h; vertical Pyrex reactor	(Rutkowski & Kubacki, 2006; Uzoejinwa et2018)
High density polyethylene	Patato skin	400cm3/min; 30min;stainless steel retort	(Önal et al., 2012; Uzoejinwa et al., 2018)
Polystyrene	Pine wood sawdust	Temperature at 450°C;5°C/min; vertical Pyrex reactor	(Rutkowski, 2009; Uzoejinwa et al., 2018)
Polyethylene	Beech wood	Temperature at 650°C; fixedbed reactor	(Kumagai et al., 2016; Ryu et al., 2020)
High density polyethylene	Almond shell	Temperature at 550°C; fixedbed reactor	(Önal et al., 2014; Ryu et al., 2020)
High density polyethylene	Sugar Bagasse	Temperature at 400-700°C;fixed bed reactor	(Hassan et al., 2020; Ryu et al., 2020)
Polystyrene	Grape seeds	Temperature at 550°C; fixedbed reactor	(Ryu et al., 2020; Sanahuja-Parejo et al., 201
Polystyrene, Polyvinyl chloride	Poplar wood	Temperature at 750°C; fixedbed reactor	(Ephraim et al., 2018; Ryu et al., 2020)
Polyethylene terephthalates, Polystyrene, Polyvinyl chloride	Walnut shell	Temperature at 500°C; fixedbed reactor	(Ryu et al., 2020; Yu et al., 2019)

Waste tire	Cotton stalk	Temperature at 550°C; fixedbed reactor	(Ryu et al., 2020; Shah et al., 2019)
Polypropylene, Polyethylene terephthalates, Polyvinyl chloride	Paulownia wood	Temperature at 50-1000°C;heating rate 10,20& 40°C min; TGA instrument	(Chen et al., 2017)
Low density polyethylene	Pubescens	Temperature at 450-470°C;fixed bed reactor	(Liu et al., 2014; Uzoejinwa et al., 2018)
Low density polyethylene, Polypropylene Polystyrene	Olive residue	Temperature at 27-1000°C;heating rate of 2,10,20 and 50K/min; TGA instrument	(Aboulkas et al., 2009; Uzoejinwa et al., 201
Low density polyethylene, Polypropylene Polystyrene	Timber	Temperature at 700-900°C;stainless tubular reactor	(Ohmukai et al., 2008; Ryu et al., 2020)
Waste polystyrene Foam	Pine sawdust	Temperature at 500°C;bubbling fluidized bed reactor	(Van Nguyen et al., 2019)

8. Thermal analysis techniques

Thermal analysis involves a group of techniques which record the change in the physical property of a substance as a function of temperature, under a controlled temperature programmed (Attia et al., 2013). Thermogravimetric analysis (TGA), Differential scanning calorimeter (DSC) and Differential thermal analysis (DTA) are main thermal investigation methods, adopted to examine the thermal degradation of substance and also for estimation of kinetics parameters (White et al., 2011).

8.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is one of the simplest methods used to computing the weight loss of a sample with respect to time and temperature. It is also for explore the thermal decompositions and kinetics of pyrolysis method for solidified substances (Chattopadhyay et al., 2008). Differential thermo gravimetric analysis (DTG) is the first derivative of the weight loss in relation to temperature and time (Yahiaoui et al., 2015). TGA has various advantages such as simple to run, require minimum amount of feedstock, continuously computes of temperature and sample weight loss (Saldarriaga et al., 2015). Furthermore, it has potential to consolidate with other analytical tools likes Gas Chromatography and Fourier transform infrared or Mass Spectrometer (Bahng et al., 2009).

8.2 Thermal analysis of biomass

Figure 2 represents Thermogravimetric analysis (wt.%) as well as Differential thermogravimetric analysis (wt.%/°C) curves of cellulose, hemicelluloses, and lignin, which reveals that all the three components shown different thermal behavior. They start to decompose at different temperature under same condition. The decomposition of hemicelluloses starts first and their highest weight loss is observed in the temperature range of 210-320°C with the highest mass loss rate (0.95 wt%/°C) at 268°C. Cellulose starts to decompose at a high temperature. Its maximum weight loss is observed in a narrow temperature scale (320–410°C) with the maximal weight loss rate (2.9 wt%/°C) at 360 ºC. The decomposition of lignin slowly happens at temperatures in the middle of 100 ºC to 900 ºC with an extremely modest mass loss rate (<0.15 wt% / °C).

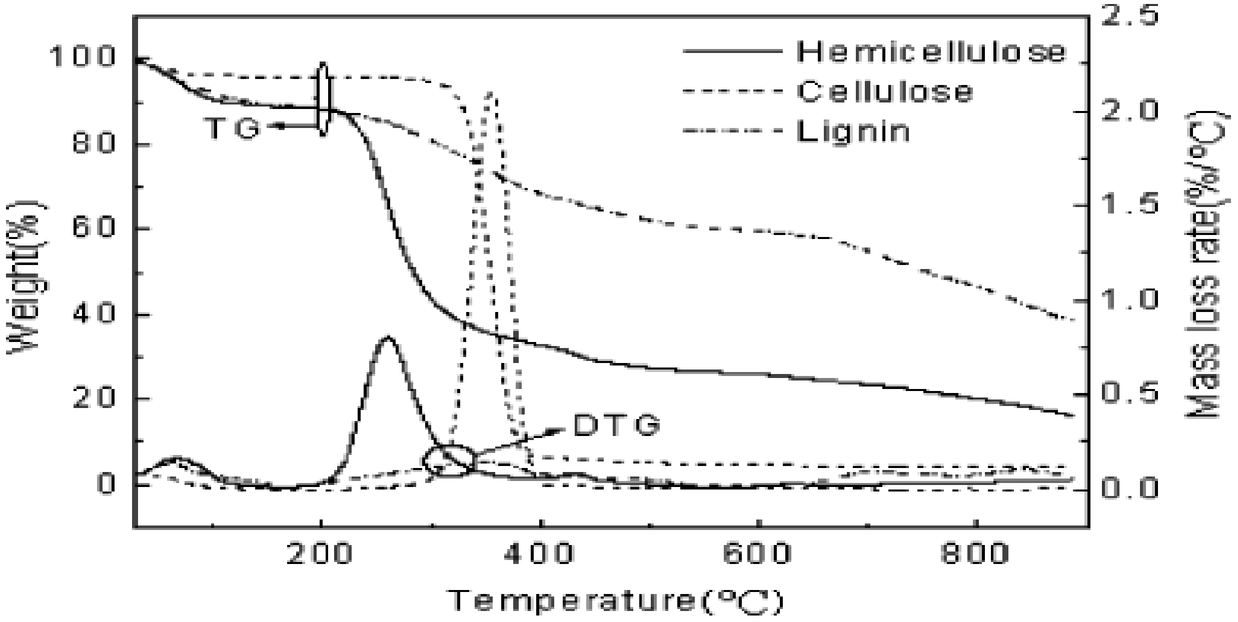


Figure 2. TG and DTG curve of pure hemicellulose, cellulose and lignin (H. Yang, 2007).

9. Kinetic Study

Co-pyrolysis of biomass and plastic appears like a completely complicated method due to the varieties in chemical composition of both biomass and plastic. Furthermore, their thermal deterioration is also happening simultaneously in co- pyrolysis; hence, its estimation about the definite response operation is not possible. However, the co- pyrolysis response of biomass and plastic may be expressed in general form by Equation (1) (Mishra & Mohanty, 2018; Varma et al., 2021a).Biomass/wastes (solid) → volatiles (gases + tar) + char (solid residue)
(1)

There are numerous techniques accessible to estimate the kinetic variables; generally, every kinetic version followsArrhenius equation which is described by the following equations:

$$K(T) = Ae^{\frac{-E_a}{RT}} \quad (2)$$

Where,
K(T) = Reaction rate coefficient
A = Pre-exponential factor or frequency factor (per minute)Ea = Energy of activation (kilo Joule per mol),
R = Molar Gas Constant (8.314 Joule per mol per Kelvin)T = Absolute Temperature (Kelvin)
The rate of reaction from solidified to volatile substance is described by the following rate equation

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (3)$$

Where,
$\frac{d\alpha}{dt}$ =Conversion rate of reactant,
T = absolute temperature,
f(α) = mass dependent reaction model,a = degree of conversion,
t = conversion time (Rego et al., 2020).
The degree of conversion may be expressed in the following form:

$$\alpha = \frac{m_o - m_i}{m_o - m_f} = \frac{V}{V_f} \quad (4)$$

Where, m_o, m_f, m_i, are the initial mass, final mass and the mass of the sample present at any time t; V is the mass of volatiles present at any time t, V_f is total mass of volatile evolved during the reaction. The fundamental expression can be obtained by replacing Equation (2) in Equation (3), Equation (5) can be derived which is used to determine kinetic parameters.

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}}f(\alpha) \quad (5)$$

Under the non-isothermal thermogravimetric evaluations, temperature is a function of time and it increases with constantheating rate (β) is expressed as

$$\beta = \frac{dT}{dt} = \frac{d\alpha}{dt} \times \frac{dT}{d\alpha} \tag{6}$$

For non-isothermal process the following equation can be used:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \times \frac{dt}{dT} \tag{7}$$

Where, $\frac{d\alpha}{dT}$ is rate for the non-isothermal reaction and $\frac{d\alpha}{dt}$ is rate for the isothermal reaction.

By using Equation (6) and (7) the rate equation can be obtained as follows:

$$\frac{d\alpha}{dT} = \frac{K(T)}{\beta} f(\alpha) = \frac{A}{\beta} e^{\frac{-E_a}{RT}} f(\alpha) \tag{8}$$

Equation (8) shows the general form of the iso-conversional methods with constant heating rate (I. Ali et al., 2018). The rate equation in differential form can be showed as:

$$ln\left({}^{d\alpha}/_{dt}\right) = ln\left(\beta \frac{d\alpha}{dT}\right) = ln[Af(\alpha)] - \frac{E_a}{RT} \tag{9}$$

The integral form of the rate equation can be obtained by integrating and rearranging the Equation (8), gives the following expression

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{Ae^{\frac{-E_a}{RT}}}{\beta} dT = \frac{AE_a}{\beta R} \int_0^\infty u^{-2} e^{-u} du = \frac{AE_a}{\beta R} p(x) \tag{10}$$

Here, p(x) is temperature integral form and g(α) is an integral form of reaction model, $X = \frac{E_a}{RT}$, the temperature integral P(x) has no exact solution, however, it can be solved by either numerical integral methods or approximations (Varma et al., 2021a; Varma & Mondal, 2016).Pyrolysis kinetics models for non-isothermal experiment

For planning, advancement and increasing to modern plant level, a real comprehension of pyrolysis kinetics is needed to accomplish the best energy recuperation (Özsin & Pütün, 2017). Numerous techniques exist for non-isothermal evaluation of solidified material via thermogravimetric analysis which may be separated into 2 sorts: the model-fitting technique and the model-free technique for the assessment of kinetic parameters (Santos et al., 2013). There are a few techniques accessible for examining TGA information. In model-fitting, reaction models must be assumed first and the model which gives best regression fit were select as a most appropriate reaction model from which the activation energy and pre-exponential factor can be computed. Iso-conversional (multi-heating) techniques have the ability to estimate complex response of materials. The model-free techniques are basic in nature, and greatest benefits are that there is no threat to choose a incorrect kinetic model and to find kinetic parameters (Mishra et al., 2019). These techniques don't need any previous information on the response system correction scheme. Iso-conversional without model techniques depend on the way that the response rate at a specific conversion degree (αi) during a specific heating rate (βi) is just an element of temperature (T) though f(α) stays consistent. In this manner the temperature dependence of the iso-conversional rate is utilized to assess the activation energy (E) an at a specific conversion (I. Ali et al., 2018).

10.1 Iso-conversional (model-free) methods

10.1.1 Friedman method

The Friedman method (Friedman, 1964) is the greatest ordinary differential iso-conversional practice for figuring out the activation energy as a function of conversion factor. It is found on the premise that the breaking down of the solids reliant only on the rate of mass loss and is free of the temperature. For determining of kinetic parameters the final differential equation derived by Friedman can be expressed as (**S.** Singh et al., 2021; Wu et al., 2013);

$$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln[Af(\alpha)] - \frac{E_a}{RT} \qquad (11)$$

for given conversion degree, the activation energy can be estimated from the slope of the straight line by plotting $\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right]$ vs. $-(RT)^{-1}$

(Olajire et al., 2014; Yao et al., 2020).

10.1.2 Ozawa–Flynn–Wall (OFW)

Ozawa–Flynn–Wall (OFW) practice is mainly applied for finding kinetic variable of substance. This method used Doyle’s estimation that is $\log p(x) = -2.315 + 0.457x$ for $20 \leq x \leq 60$ to determine kinetics parameters the final equation can be expressed as (Huang et al., 2016; Science et al., 1983);

$$\log \beta = \log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.315 - 0.457\frac{E_a}{RT} \qquad (12)$$

The plot between log β versus $-0.457\,(RT)^{-1}$ will provides straight line whose slope is employed to find out activation energy (Mishra & Mohanty, 2020).

10.1.3 Kissinger

Kissinger developed a non-isothermal model-free method in which it is never mandatory to compute the activation energy for every transformation value to compute the kinetic variables; i.e., not all model-free techniques are iso-conversional. For determining the activation energy the final equation can be expressed as (Santos et al., 2013).

$$\ln\left(\frac{\beta}{T_m{}^2}\right) = \left\{\ln\frac{AR}{E_a} + \ln[n(1-\alpha_m)^{n-1}]\right\} - \frac{E_a}{RT_m} \qquad (13)$$

Here, “T_m"= temperature value of the maximum reaction rate, “α_m"= transformation value at the maximum reaction rate. The plot between $\ln\left(\frac{\beta}{T_m}\right)$ versus $\frac{1000}{T}$ allows straight line whose slope might be adopted to figure out activation energy (Santos et al., 2013; Sources et al., 2020).

10.1.4 Kissinger–Akahira–Sunose (KAS)

Kissinger–Akahira–Sunose is an integral model-free method which is widely applied to figure out kinetic energy of material. These method used Doyle’s approximation (Doyle,1965), to get final equation to estimate activation energy can be expressed (Kaur et al., 2018) as

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{g(\alpha)E_a}\right) - \frac{E_a}{RT}$$

(14)

Kinetic plot between $\ln\left(\frac{\beta}{T^2}\right)$ versus $(RT)^{-1}$will provide slope and intercepts adopted for estimation of activation energy and frequency factor(Mishra & Mohanty, 2018; Sources et al., 2020).

10.1.5 Starink

The Starink is an iso-conversional model, employed for find out activation energy of biomass through pyrolysis and co-pyrolysis. The values of activation energy are determined from the slopes of the linear plots arranged using respective models at α = 0.1 to 0.9 and the final equation can be expressed as

$$\ln\frac{\beta}{T^{1.92}} = -1.0008\frac{E_a}{RT} + \text{Constant}$$

(15)

Kinetic plot between $\ln\left(\frac{\beta}{T^{1.92}}\right)$ versus $\frac{1}{T}$ will offer a straight line and slope $-1.0008\frac{E_a}{R}$ adopted for calculation of

energy(M. Kumar et al., 2020; Özsin & Pütün, 2017; Sahoo et al., 2021; Yao et al., 2020).

In past work, a so many specialists utilized iso-conversional model-free technique to compute the kinetics parameter of various biomasses for pyrolysis operation. The mean activation energy of various biomass and plastic determined by various iso- conversional techniques are represented in **Table 5**.

Table 5. Activation Energy of different biomass with plastic calculated by OFW, KAS, Friedman, along with Starink

methods.

Biomass	**Plastic**	**Activation energy, E_a KJmol^{-1}**				**References**
		OFW	**KAS**	**Friedman**	**Starink**	
Pine needles	Styrofoam	109.73	96.44	-		(Varma et al., 2021b)
Bamboo Saw dust	Linear Low-Density Polyethylene	400.00	371.00	356.00	-	(Bhavanam, n.d.)
Corn cob	Polyethylene	216.00	216.00	221.00	216.00	(S. Singh et al., 2021)
Walnut shells	Polystyrene	201.00	223.8	238.6	200.6	(Özsin & Pütün, 2017)
Peach stones	Polystyrene	224.5	-	-	223.1	
Torrefied Bamboo Saw	Linear Low-Density Polyethylene	216.00	264.00	254.00	-	(Alam et al., 2021)
SamaneaSaman seed	Polyethylene terephthalate	168.57	166.98	178.50	166.96	(Mishra et al., 2019)
Mahua seeds	Waste thermacoal	-	-	171.44	-	(Pradhan et al., 2020)

10. Conclusion

Complete knowledge of the properties of the biomass and polymer provide valuable informations about the common characteristics of both and its potential for utilization. The proximate analysis describes the quality of biomass and plastic for further conversion and processing. Thermogravimetric analyzer (TGA) is found an effective tool to analyze the thermal behavior of material and data obtained using such analysis are used to determine kinetics parameters. TGA provide easy, quick, and reliable technique for carrying out any kinetic analysis. The methods which are generally utilized for estimation of kinetics parameters of pyrolysis are mainly model-free and model-fitting. Iso-conversional model-free methods are widely used to calculate the co-pyrolysis kinetics parameters. Friedman, Kissinger, Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose, Starink are the main iso-conversional methods used to compute kinetics parameters. Knowledge of the co-pyrolysis kinetics parameters of thermal degradation of lignocellulosic biomass materials and plastics waste provides useful information for the outlook of reaction conduct and also for the planning and optimization of reactors. As a conclusion, in this study showed that, by using thermal pyrolysis of biomass with synthetic polymer could be an environmentally friendly way for the reduction in pollution and conversion of plastic waste and lignocellulosic into the beneficial products and thus promoting to a sustainable energy source. Furthermore, this study provides the information of process parameters of co-pyrolysis and the activation energy, which can be further used for industrial application.

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