

A Review on Biofuels and Chemicals Production by Co-pyrolysis of Solid Biomass Feedstocks and Non-degradable Plastics

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Abstract

Modern lives have resulted in a substantial rise in the volume of plastic waste in recent years. Throughout, there is a lot of solid biomass that can be used as energy. By co-pyrolysis, these waste plastic and solid biomass feedstock mixes can be transformed to produce synergistic fuels and value-added products. To promote environmentally appropriate pathways for waste management and sustainability, the manufactured products can be used as chemicals and pollutant sorbents. This review's main focus is on the advancement of this method of waste disposal and energy production. The difficulties and potential benefits of developing combinations of solid organic waste and plastic feedstock for co-pyrolysis are also covered. With the introduction of waste biomass for improved synergistic effects in waste disposal as well as the recovery of energy and value-added products, the objective was to provide attractive practicable pathways for clean and efficient disposal of plastic wastes.

Keywords: Catalytic co-pyrolysis, liquid products, gas products, solid products, waste plastic, solid biomass, co-pyrolysis, mix ratio, synergistic effect

1. Introduction: Due to the relatively sluggish pace of technical advancement, solid waste management is one of the most significant global concerns facing humanity today. With the development of odours and by products that are harmful to the environment and have an influence on human health, the practise of landfills is unsustainable and expensive in terms of environmental costs [1]. Increasing usage of solid organic wastes can offer valuable underutilised negative cost resources that can be turned into energy to address concerns with energy needs as well as waste management and disposal [2]. Research to achieve environment protection, waste management, and energy production may be centred on the combination of environment, resources, and energy. Ease in processing, low cost, light weight, continuity, and chemical and environmental erosion resistance handed by plastics have led to their rapid-fire growth over the once 50 times to make them a ubiquitous element in a wide range of goods including product of consumer goods(3). still, low degradability of the plastics causes serious environmental problems and a big challenge in waste operation(4). According to the United States Environmental Protection Agency(EPA), while 35.4 million tons of plastic wastes were generated in 2017 in the USA, only 75.8 of this quantum were landfilled. The quantities generated and landfilled in 2015 were also analogous(,6). Amounts of plastic waste generation and disposal in colorful regions of the global, including the USA, as well as their estimated growth from 1950 to 2050 are shown in Fig 1(a)(7). In 2018, plastics product

reached 359 million tons encyclopedically(Fig. 1 (b)), out of which China contributed to 30 of the world’s plastics product, and Europe’s plastics product reached nearly 62 million tons(contributing to 17)(8). It’s estimated that with the current rate of waste operation the plastic generation will affect in roughly 12 billion metric tons of waste disposal into tips or into some other natural coffers by 2050(7). indecorous disposal of waste plastics including landfilling can lead to their structural decomposition with time into lower patches of different sizes that includesmacro-plastics, meso- plastics,micro-plastics, and nano-plastics. Micro-plastics are small plastic patches lower than five millimeters(9), which can convey as adulterants via water and fodder into food to affect mortal health and the ecosystems by entering into food chain in addition to deteriorating agrarian soils(10 – 12). Oceanic plastic pollution is also a growing problem worldwide to beget environmental concern and venturing multitudinous marine species(13).

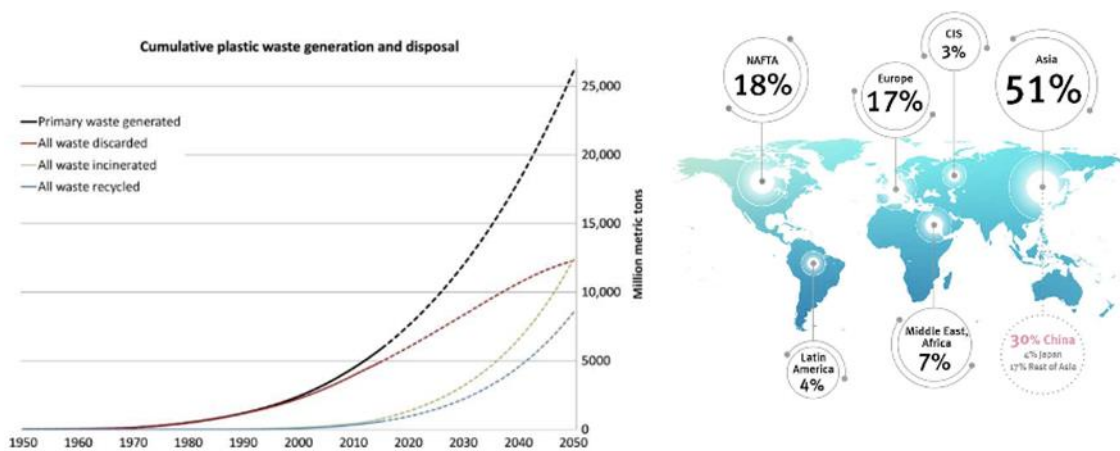


Fig. 1. Global plastic waste generation and distribution. (a) Cumulative plastic waste generated and their disposal [7]. (b) Distribution of global plastics production in 2018 (Polyethylene Terephthalate (PET)-fibers and Polyacryl (PA)-fibers were not included) [8].

Although the below sense make landfilling monstrous, incineration is extensively accepted because it can permanently putrefy plastic waste that also offers high volumetric reduction and thermal energy recovery that can latterly be used for conversion to electrical energy. Incineration also provides carbon operation in the regular energy product sector by displacing other energies used for product(,15). Significant number of incineration shops use plastic wastes that were developed in Europe(15). still, incineration of these wastes causes release of poisonous adulterants similar as phosgene, dioxins, polycyclic sweet hydrocarbons, polychlorinated biphenyls, heavy essence, poisonous free revolutionaries, and dust that are dangerous to the ecosystem as well as pitfalls of carcinogenic, mutagenic, and neurological complications to humans(,17). Emission of airborne adulterants can beget impurity near to the vicinity of the combustion unit, thereby affecting conterminous communities with

unwelcome odors and poisonous emulsion emigrations, which can beget adverse goods to health, property and structure aesthetics(18). The incineration requires expansive stovepipe- gas cleaning, which leads to significant increase in costs, reduced process effectiveness and therefore unsustainable operation, especially in terms of energy recovery and environmental impact.

To avoid the resource destruction and terrain pollution, numerous strategies have been proposed to use the waste plastics, especially for energy and energies product. A better pathway to resolve these issues is by thermal corruption with controlled oxidation due to benefits on lower contaminant’s emigration, give product uniformity, high outturn, scalability, effectiveness, and feedstock versatility as compared to other

processes similar as, anaerobic digestion and other chemical and biochemical conversion ways(20). Thermochemical disposal ways similar as pyrolysis and gasification can give effective and protean recovery for energies and value- added chemicals from the plastic wastes with better outturn as compared to biochemical processes(2). The colorful types of solid waste give not only unique challenges for energy application, but also the energies and energy yield from gasification or pyrolysis as they're explosively told by the mixed feedstock composition and bit(22). Pyrolysis is the thermal corruption of organic substances in the absence of oxygen to form liquids(condensable), solids, and non-condensable feasts(24). Fast pyrolysis at moderate temperatures and veritably short response times has gained considerable interest in the recent decades for its capability to widely produce bio-oil products(25). The pyrolysis of pure plastics can give pyrolysis oil painting and syngas with bettered hydrogen content and spicy value along with lowered oxygen content to affect in bettered oil painting parcels. These processes are prone to scalability issues in terms of congesting the feedlines due to high density of melted or softened plastics in addition to the problem of inhibited fluidization(25). Coking was also observed in these reactors, which led to downstream blockages and dropped products yield and quality, and increased functional difficulties. likewise, acquiring and separating out the waste plastics into pure factors is delicate due to lack of proper structure for waste separation with the current large reliance on homemade separation. This leads to plastics wastes frequently supplied as part of external solid wastes that are defiled or mixed with other plastic or bio-wastes. So, understanding the conduct and development of co-pyrolysis processes is essential as it not only relaxes the need for waste separation but also offers some pledge of barring functional issues in pure plastic waste conversion(26).

Biomass and biowastes are formed via photosynthetic routes using uprooted solar energy to sequester CO₂ and H₂O in the form of carbonaceous solids. Due to fairly fast product rate of biomass and its carbonaceous nature, it's considered carbon neutral when converted to protean products(27). The products from biomass can range from energy precursors(similar as syngas, liquid bioethanol, liquid biodiesel, solid briquette, gassy methane, and biodegradable plastics) to biochemical products, which are analogous to the counterpart reactionary- energy incumbents(28). Bioenergy is the only form of renewable energy that can be collected, stored, and transported, and this form of renewable energy is most analogous to conventional reactionary energy energy sources(30). thus, the bioenergy is dispatachable energy and can be used when asked . Figure 2 shows special characteristics and products of biomass energy in a renewable energy system. Biomass coffers astronomically includes colorful sources, similar as wood or timber remainders(e.g., tree branches, leaves, shrubberies, lawn), agrarian grain remainders(e.g., straw, stalk, sludge cob), energy fraternity(e.g. jatropha curcas seed, switchgrass, algae), food product or assiduity remainders and derivations(e.g., coffee nut shell, other nut shell), beast husbandry(e.g., ordure that's rich in nitrogen and phosphorus, beast fat), mortal waste from sewage shops and external shops(31). Solid biomass reckoned for the largest share of biomass application in the form of heat and electricity(32). In 2017, artificial heat energy consumption from solid biomass was roughly 898 PJ in the European Union with dominant benefactions in pulp, paper and printing, as well as in the wood and wood products diligence, which reckoned for some 85 of the biomass energy consumption in the artificial sector(33). Solid biomass for energy application can be attained from different kinds of organic remainders including forestry remainders, agrarian remainders, energy shops or crops, artificial organic wastes or remainders, and external solid wastes. It's substantially used directly in the form produced by the assiduity(e.g., sawdust, forestry and agrarian chips), but occasionally upgraded in the form of solid biofuels(e.g., briquette energy, block shaped energy, densified bullet energy, biochar, torrefied biomass)(33).

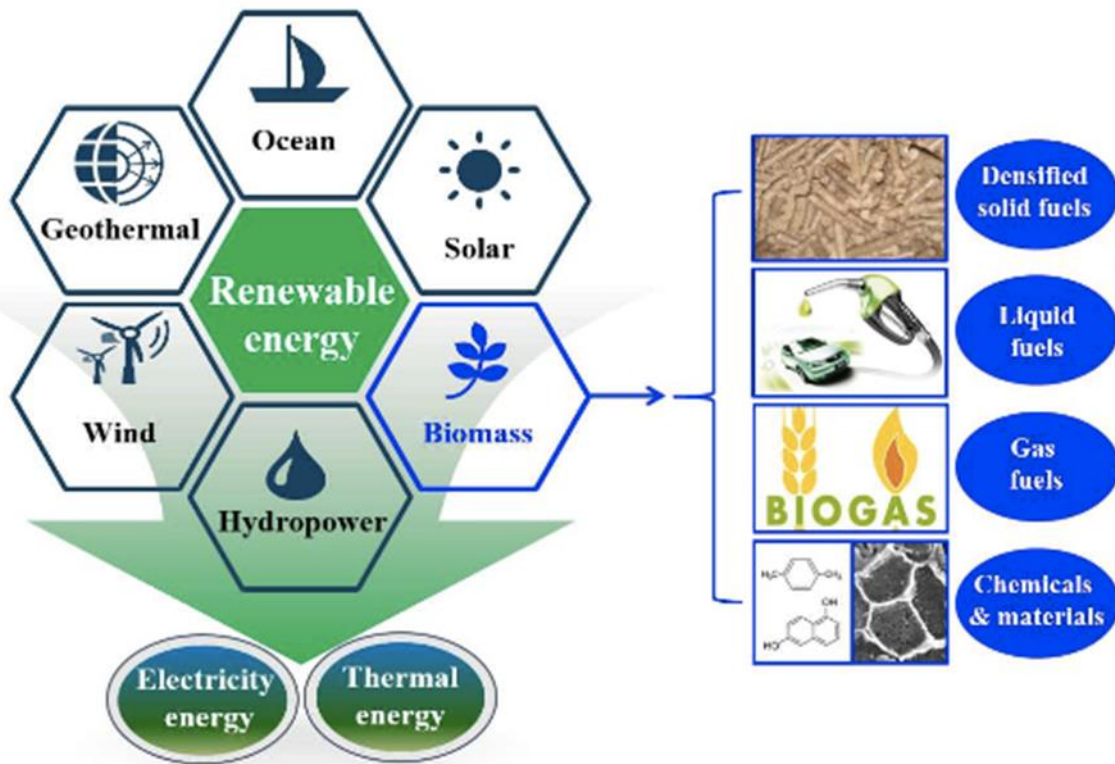


Fig. 2. Special characteristics and products of biomass energy in renewable energy system.

Co-pyrolysis of waste plastic and solid biomass led to synergistic goods, which could ameliorate products quality(34). Plastic wastes contain high hydrogen to carbon(H/ C) rate and fairly low oxygen to carbon(O/ C) rate which can support solid biomass’s innately high O/ C and low H/ C during co-pyrolysis to affect in increased quality and uniformity of the products while minimizing coke deposit displayed by pyrolysis of pure plastic wastes(35). Co-pyrolysis offers an seductive pathway with high eventuality for mixed wastes by minimizing the conditions on waste separation(36).

Co-pyrolysis studies on waste plastic and solid biomass in the recent times include abecedarian as well as review papers for studies on colorful response conditions, reactors and product yield optimization with focus on variations in kinetics(37), thermal conduct

(38), synergistic effect in products(39 – 41). Activation powers needed in co-pyrolysis of admixture was lower than that of waste plastic but advanced than that of solid biomass(37). Energy operation forco-pyrolysis of different fusions(1.43 –1.84 MJ/ kg) were advanced than solid biomass(1.29 MJ/ kg) but lower than waste plastic(2.07 MJ/ kg)(38). product of oil painting increased while the housekeeper dropped(39). Increase in housekeeper quantities was also possible depending on theco-pyrolysis conditions,(41). Abnisa etal., Hassan etal. and Zhang etal. reviewed and epitomized the exploration progress innon-catalytic and catalyticco-pyrolysis and their benefits on quality improvement of pyrolysis oil painting deduced from biomass mixed with waste plastics, waste tires and coal accoutrements during pyrolysis to produce bettered liquid energy yields(42 – 44). These studies revealed that co-pyrolysis of waste plastic and solid biomass can significantly ameliorate the yield and quality of pyrolysis oil painting(42) while catalyticco-pyrolysis of waste plastic and biomass can give superior performance in upgrading pyrolysis oil painting(43). Catalytic co-pyrolysis of lignocellulosic biomass with waste plastic to produce

aromatics can be a more promising fashion than the catalytic pyrolysis alone of lignocellulosic biomass(44). Wong et al. reviewed specialized aspects of converting plastic wastes into energy using thermal, microwave oven and catalytic pyrolysis, and fluid catalytic cracking, as well as liquids from co-pyrolysis of plastic wastes with biomass(3). Uzoejinwa et al. bandied the advantages of the co-pyrolysis process in terms of yield, medium and functional control and set up them to be promising compared to biomass pyrolysis alone(45). Block et al. reviewed literature on the co-pyro gasification of plastics and biomass from the perspective of process pathway, reactors, feedstock characteristics and operating conditions on the products distribution, along with synergetic goods between plastics and biomass fusions(26). But to be the stylish of our knowledge, streamlined and comprehensive review ofco-pyrolysis of several different kinds of plastics mixed with solid biomass at different scales of reactors as well as the distribution of evolved products is still lacking. This work provides a broader review of the state- of- the- art advances inco-pyrolysis of fusions of waste plastic and solid biomass feedstocks starting with the perspective of physical and chemical parcels of waste plastic and solid biomass. This is also followed by the influence of different plastic wastes, reactors and functional conditions on the phase- distribution and composition of products. Added discussion is also made regarding the state- of- the art in catalysts employed for co-pyrolysis. A inflow map summary of the motifs bandied in this paper is shown in Fig. 3. With the broad perspective attained from this literature review, a discussion on the challenges and openings are summarized in conclusions. The results reveal the significance of co-pyrolysis exploration and give pathways for the unborn exploration demanded to support sustainable and synergistic waste disposal.

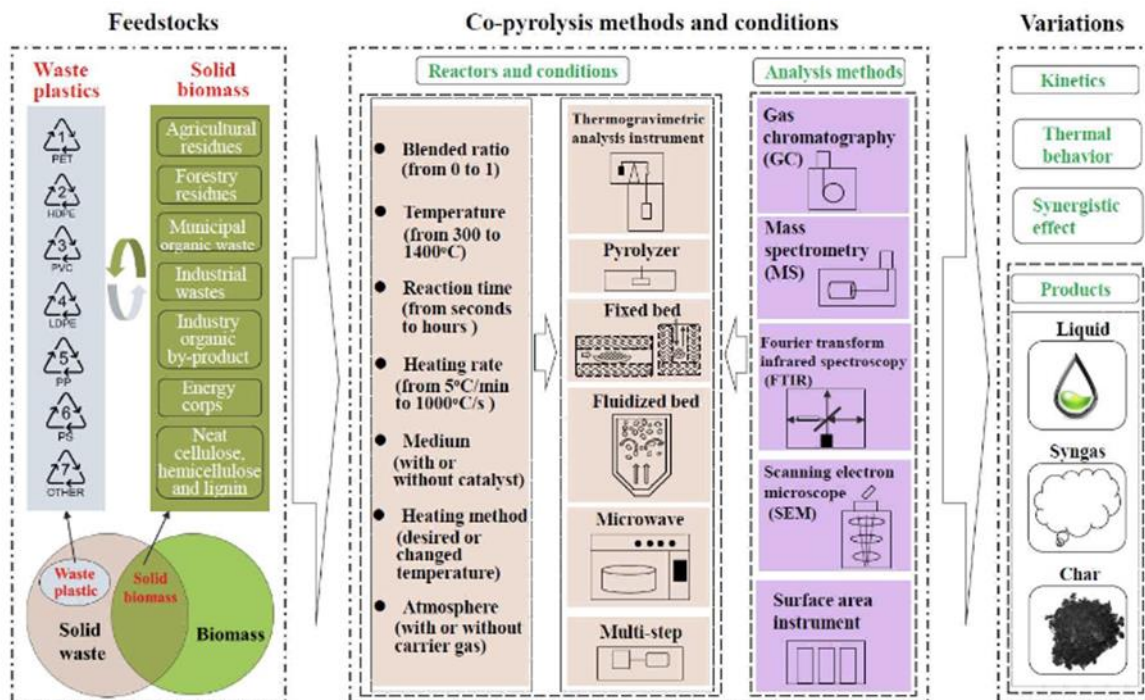



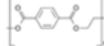











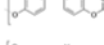



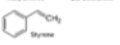
Fig. 3. Flow chart summary of lab-scale research diagnostics for co-pyrolysis of mixture of waste plastic and solid biomass.

2. Physical and chemical parcels of feedstock

2.1 Waste plastic

Plastic wastes contain different types of polymers similar as, polyethylene terephthalate(PET), high viscosity and low- viscosity polyethylene(HDPE and LDPE), polyvinyl chloride(PVC), polypropylene(PP), polystyrene(PS), polycarbonate(PC), Polyacryl(PA) and others. Although each of these plastics have different chemical structure with different quantities of carbon, oxygen and hydrogen content, their common point includes fairly high unpredictable content, density and heating value, but veritably low humidity and ash content(46). These are epitomized in Table 1 on the base of law order number(as 1, 2, 3,.) for PET, HDPE, PVC, LDPE, PP, PS, PC and others, independently(47,48).

Table 1. Commonly used plastic materials as often listed by the code number and their application

Code	Name	Abbreviation	Structural formula	Molecular formula	Application in human life	Ref.
	Polyethylene terephthalate	PET or PETE		$(C_{10}H_8O_4)_n$	Beverage bottles, food containers, films, polyester fibers for clothes, electrical parts, and other domestic applications.	[49,50]
	High-density polyethylene	HDPE		$(C_2H_4)_n$	Harder bottles, piping, toys, geomembranes, window shades and decorative board for building, etc.	[50]
	Polyvinyl chloride	PVC		$(C_2H_3Cl)_n$	Drainage pipes, electric wire and cable, window frames, floor tiles, and water piping.	[49]
	Low-density polyethylene	LDPE		$(C_2H_4)_n$	Containers, bags, soft bottles, soft tubing, ductile materials, molded materials of laboratory equipment, etc.	[50]
	Polypropylene	PP		$(C_3H_6)_n$	Drinking bottles, bottle caps, drinking straws, food containers, etc.	[49,50]
	Polystyrene	PS		$(C_8H_8)_n$	Food containers, protective packaging of household electrical appliances, bottles, building insulation, etc.	[50]
	Polycarbonate	PC		$[(CH_2)_2C(C_6H_4OH)_2]_n$ (a typical PC of all kinds)	Electronic components; construction materials such as windows and traffic lights; data storage such as compact discs, DVDs.	[46,51]
	Polyurethanes	PU or PUR		$(C_{17}H_{16}N_2O_4)_n$	Various foams, plastic walls/sheets of most refrigerators and freezers, shoes, building panel, etc.	[52]
	Acrylonitrile butadiene styrene	ABS		$(C_8H_8)_x-(C_4H_6)_y-$ $(C_7H_7N)_z$	Automotive parts, electronic appliances, household appliances, building materials, piping, etc.	[53]

The hydrogen to carbon (H/C_{eff}) ratio is an important factor affecting its potential as a fuel and value-added product. This factor shows the potential ability of the feedstock to be economically converted to hydrocarbons and also helps in estimating the overall olefins and aromatics yield, coke yield and catalyst deactivation rate [54]. Chen et al. [55] used the H/C_{eff} ratio to reflect the relative hydrogen content of different feedstocks. The H/C_{eff} ratio is based on the assumption that all heteroatoms are completely converted to H₂O, NH₃ and H₂S [56].

The H/C_{eff} ratio is calculated as follows:

$$H/C = \frac{H}{C} \quad (1)$$

where H, O, N, S and C are the mole percentages or number of moles of hydrogen, oxygen, nitrogen, sulfur, and carbon in the feedstock, respectively.

Table 2. Proximate, elemental analysis, and LHV of typical kinds of plastics.

Plastic	Proximate analysis (wt.%)				Elemental analysis (wt.%)						Heating value (MJ/kg)	Ref.	H/C _{eff}
	V	FC	A	M	C	H	N	O ^d	S	Cl			
PET	86.83	13.11	0	0.06	62.51	4.19	0	33.30	0	-	30.85 ^H	[61]	0.01
	85.0 ^a	10.6 ^a	4.4 ^a	0 ^a	66.2 ^b	4.9 ^b	0 ^b	28.9 ^b	0 ^b	0 ^b	-	[62]	0.23
	87.1	12.9 ^d	-	-	62.1	4.8	-	33.1	-	-	23.92 ^H	[63]	0.13
	89.2 ^c	10.3 ^{c,d}	0.1 ^c	0.4 ^c	62.7 ^c	4.4 ^c	0 ^c	32.8 ^c	0 ^c	-	23 ^H	[64]	0.06
	88.61	11.39	-	-	64.22	4.65	0.05	30.53	0.55	-	-	[65]	0.15
	84.1 ^a	13.9 ^a	- ^a	- ^a	64.1 ^b	3.7 ^b	-	34.2 ^b	-	-	23.97 ^L	[35]	-0.11
	83.92 ^a	13.78 ^a	1.84 ^a	0.46 ^a	62.48 ^a	4.80 ^a	0.32 ^a	-	0 ^a	-	40.34 ^G	[66]	0.91
	90.57 ^a	9.43 ^a	0 ^a	0 ^a	62.93 ^a	4.26 ^a	0 ^a	32.81 ^a	0 ^a	-	21.25 ^L	[67]	0.03
	99.46 ^a	0.00 ^a	0.34 ^a	0.00 ^a	81.45 ^b	12.06 ^b	0.34 ^b	5.36 ^{b,d}	0.79 ^b	0 ^b	-	[68]	1.66
	100 ^a	0 ^a	0 ^a	0 ^a	82.9 ^b	15.47 ^b	0 ^b	1.63 ^b	0 ^b	0 ^b	-	[62]	2.21
HDPE	100	-	-	-	85.43 ^b	14.21 ^b	0.08 ^b	0.15 ^b	-	-	38.66	[69]	1.99
	100 ^a	0 ^a	0 ^a	0 ^a	85.11 ^b	14.57 ^b	0.32 ^b	0 ^b	0 ^b	-	-	[70]	2.04
	100 ^a	-	-	-	85.86 ^b	14.14 ^b	-	-	-	-	-	[71]	1.98
	99.7	0.3	-	-	85.71	14.29	0	0	-	-	43.1 ^H	[72]	2.00
	99.9	0 ^d	0.1	0	85.5 ^c	14.5 ^c	0 ^c	0 ^c	0 ^c	-	46.4 ^H	[64]	2.04
	99.4 ^a	-	0.6 ^a	-	83.8 ^b	14.2 ^b	-	-	0.3 ^b	-	-	[73]	2.03
	97.15 ^a	- ^d	0.8 ^a	0	86.5 ^b	15.1 ^b	-	-	0.25 ^b	-	43.01 ^L	[35]	2.09
	100	0	0	0	85.4	14.6	-	-	-	-	-	[74]	2.05
	94.9 ^a	5.1 ^a	0 ^a	0 ^a	39.6 ^a	4.9 ^a	0.5 ^a	0 ^a	1.8 ^a	53.2 ^a	-	[39]	1.42
	96.41	3.42	0	0.17	38.19	4.94	-	-	-	47.66	21.66	[75]	1.55
PVC	95.8 ^c	4.2 ^c	0 ^c	0 ^c	38.7 ^b	4.8 ^b	0 ^b	0 ^b	0 ^b	56.5 ^b	19.3 ^L	[76]	1.49
	94.93 ^a	5.07 ^a	0 ^a	0 ^a	38.34 ^a	4.47 ^a	0.23 ^a	-	0.61 ^a	56.35 ^a	20.83 ^H	[77]	1.37
	-	-	-	-	39.66 ^a	5.24 ^a	0 ^a	-	0 ^a	55.04 ^a	20.38 ^L	[49]	1.59
	94.7 ^a	5.1 ^a	0.04 ^a	0.2 ^a	39.5 ^a	4.9 ^a	0.5 ^a	-	1.8 ^a	53.2 ^a	20.66 ^G	[78]	1.42
	94.78 ^a	5.06 ^a	0 ^a	-	38.56 ^a	4.6 ^a	0 ^a	0 ^a	0.4 ^a	57.04 ^a	19.88	[79]	1.42

	88.95 ^a	8.67 ^a	2.36 ^a	0.02 ^a	38.80 ^a	5.14 ^a	0.09 ^a	-	-	53.61 ^a	-	[80]	1.58
	94.75 ^a	5.25 ^a	0.64 ^a	-	38.15 ^b	4.35 ^a	0.16 ^a	-	0.45 ^a	56.25 ^a	-	[81]	1.35
	94.78 ^a	5.06 ^a	0 ^a	0.16 ^a	38.34 ^a	4.47 ^a	0.23 ^a	-	0 ^a	56.96 ^a	-	[82]	1.38
	100 ^a	0	0	0	82.18 ^b	16.37 ^b	0 ^b	1.45 ^b	0 ^b	0 ^b	-	[62]	2.36
	99.7 ^a	-	0.3 ^a	-	85.5 ^b	14.3 ^b	-	-	0.2 ^b	-	-	[73]	2.01
	99.9	-	0.1	-	85.9	14.0	-	-	-	-	43.1 ^{II}	[83]	1.96
LDPE	100 ^a	0 ^{a,d}	0 ^a	-	85.7 ^b	15.3 ^b	0 ^b	0 ^b	0 ^b	-	-	[84]	2.02
	99.08 ^a	0 ^a	0.02 ^a	0 ^a	86.35	13.58	0	0	0.074	-	46.15	[85]	1.89
	99.7 ^b	0.3 ^b	0.3 ^a	-	85.2 ^b	14.1 ^b	-	0.5 ^b	0.2 ^b	-	-	[86]	1.98
	100	0	0	-	85.46	13.54	0	1.00	-	-	-	[87]	1.88
	100 ^a	0 ^a	0 ^a	0 ^a	85.1 ^b	13.38 ^b	0 ^b	1.52 ^b	0 ^b	0 ^b	-	[62]	1.86
	100	0	0	0.08	84.80	14.55	0.14	0.28	0.23	-	45.80 ^{II}	[61]	2.05
	99.8 ^c	0 ^{c,d}	0.1 ^c	0.2 ^c	85.4	14.5	0	0	0	-	46.0 ^{II}	[64]	2.04
	98.9 ^a	-	1.1 ^a	-	83.8 ^b	13.9 ^b	-	-	2.3 ^b	-	-	[73]	1.97
PP	96.9 ^a	- ^d	1.0 ^a	0 ^a	84.7 ^b	15.3 ^b	-	-	2.1 ^b	-	45.08 ^L	[35]	2.15
	93.84 ^a	2.04 ^a	3.68 ^a	0.44 ^a	83.28 ^a	13.81 ^a	0.01 ^a	-	0.01 ^a	-	44.43 ^G	[66]	1.99
	98.54 ^c	-	1.06 ^c	0.40 ^c	83.74 ^b	13.71 ^a	0.02 ^a	0.98 ^a	0.08 ^a	-	-	[88]	1.95
	99.6 ^c	0.1 ^c	0.2 ^c	0.1 ^c	86.5 ^b	12.9 ^b	0.3 ^b	-	0.3 ^b	-	37.6 ^{II}	[89]	1.78
	99.85 ^a	0 ^a	0.15 ^a	0 ^a	85.03 ^b	14.80 ^a	0 ^a	0 ^a	0 ^a	-	42.80 ^{II}	[80]	2.09
	100 ^a	0 ^a	0 ^a	0 ^a	91.2 ^b	8.8 ^b	0 ^b	0 ^b	0 ^b	0 ^b	-	[62]	1.16
	100 ^a	-	<0.3 ^a	-	90.9 ^a	7.7 ^a	<0.1 ^a	1.4 ^{a,d}	-	-	-	[90]	>0.99
	99.58	0.05	0.09	0.29	92.12	7.88	-	0.01	-	-	-	[38]	1.03
	99.5	0.5	-	-	92.2	7.8	-	-	-	-	-	[91]	1.02
	99.12 ^a	0.39 ^a	0.04 ^a	-	92.16 ^a	7.72 ^a	0 ^a	0 ^a	0.26 ^a	0.36 ^a	37.45	[79]	1.00
PS	99.76	0.24	0	0	92.04	7.29	0	0.67	-	-	-	[87]	0.94
	94.33 ^a	4.55 ^a	0.28 ^a	0.84 ^a	89.2 ^a	8.78 ^a	0.01 ^a	-	0 ^a	-	40.34 ^G	[66]	1.18
	97.71 ^c	0.45 ^c	0.98 ^c	0.86 ^c	90.34 ^b	9.06 ^b	0.29 ^b	0.31 ^b	-	-	43.58	[92]	1.19
	98.8 ^a	0 ^a	0.3 ^a	0.2 ^a	90.4 ^b	8.6 ^b	0.4 ^b	0.6 ^b	-	-	42.3 ^{II}	[93]	1.12
	99.24 ^a	0.02 ^a	0.24 ^a	0.50 ^a	90.55 ^a	7.82 ^a	0.17 ^a	0 ^a	1.22 ^a	-	38.60 ^{II}	[80]	1.02
	99.12 ^a	0.39 ^a	0.04 ^a	0.45 ^a	86.06 ^b	6.27 ^a	5.73 ^a	1.93 ^a	0 ^a	-	-	[82]	0.67
PC	80.47	19.48	0.05	0	75.71	5.47	0	18.82	-	-	30.08 ^{II,c}	[87]	0.49
PU	83.20 ^a	10.60 ^a	6.20 ^a	-	62.69	6.32	6.37	24.01	0.63	-	26.03 ^{III,e}	[41]	0.37
ABS	100.00	0	0	0.05	75.44	8.19	4.74	3.44	8.19	-	38.09 ^{II}	[61]	0.99

[Proximate analysis] V: volatile; A: ash; FC: fixed carbon; M: moisture.

[Elemental analysis] C: carbon; H: hydrogen; O: oxygen; N: nitrogen; S: sulfur; Cl: chlorine.

[Heating value] ^{II}: higher heating value; ^L: lower heating value; ^G: gross heating value.

^a: dry basis; ^b: dry ash free basis; ^c: received; ^d: by difference; ^e: calculated; -: not reported.

Higher heating value of PC and PU were calculated by formula of HHV=33.82*C+144.25*(H-O/8) + 9.42*S (MJ/kg).

Antioxidants, ultraviolet (UV) stabilizers, plasticizers, heat stabilizers, lubricants, photoinitiators, antistatic agents, etc. are added during plastic manufacturing to improve and maintain the properties of the polymer. This can lead to discrepancies between theoretically pure plastic compositions and industrial elemental analyses, as these additives are unknown and their addition can change the net raw material composition by 0.02% to 0.5% [57,58]. Table 2 lists the actual elemental and approximate analyzes and LHV's for some typical plastic materials.

During pyrolysis or gasification, plastics can be co-pyrolyzed with biomass as a pool of hydrocarbons, producing a large amount of H₂ and H⁺ during the pyrolysis process. The amounts of C and H of the feedstock and the oil as well as the H/C ratio are significantly related to the calorific value of the pyrolysis oil produced. The availability of hydrogen during co-pyrolysis improves the quality of pyrolysis oil from biomass-plastic mixtures [59,60].

2.2 Solid Biomass

Solid biomass covers a wide range of materials, including wood, straw, agricultural residues, processing wastes, algae and seaweed [94]. Solid biomass can also be obtained from livestock manure, municipal organic solid waste; the latter is a suitable raw material for pyrolysis. Elemental analysis, industrial analysis and LHV of typical solid organic biomass materials suitable for co-pyrolysis are shown in Table 3.

Table 3. Proximate, elemental analysis, and LHV of characteristic solid biomass in co-pyrolysis.

		Proximate analysis (wt.%)				Elemental analysis (wt.%)					Heating value (MJ/kg)	Ref.	H/C _{eff}
		V	FC	A	M	C	H	N	O ^d	S			
Agricultural residues	Corn stalk	73.8 ^a	15.0 ^a	5.8 ^a	5.4 ^a	47.5 ^b	6.1 ^b	0.8 ^b	45.6 ^b	-	15.7 ^{HI}	[93]	0.06
	Rice straw	66.2 ^c	8.2 ^c	15.1 ^c	10.5 ^c	52.3 ^b	7.3 ^b	1.3 ^b	38.5 ^b	0.1 ^b	19.7 ^{HI}	[89]	0.51
	Tobacco stalk	71.31 ^a	20.17 ^a	8.52 ^a	-	41.09 ^a	5.02 ^a	2.42 ^a	42.75 ^a	0.21 ^a	-	[81]	-0.25
	Cotton stalk	64.92	22.10 ^d	5.52	7.46	47.95 ^b	5.50 ^b	3.24 ^b	43.31 ^b	-	16.3	[37]	-0.15
Forestry Residues	Sun flower residues	65.26	19.35 ^d	6.72	3.02	47.91 ^b	5.27 ^b	8.65 ^b	38.17 ^b	-	16.9	[37]	-0.34
	Pine wood	85.6	14.2	0.2	-	48.72	6.52	0.23	44.41	0.12	17.65 ^{LI}	[95]	0.22
	Bamboo	83.95 ^b	16.05 ^b	1.95 ^m	6.14 ^b	50.52	6.04	0.58	>42.80	0.09	17.87 ^{GI}	[96]	<0.13
	Beech wood	80.2 ^c	12.4 ^c	0.4 ^c	7.0 ^c	49.9	6.2	-	43.9	-	-	[97]	0.17
	Yellow poplar	86.2	13.3	0.1	0.5	47.8 ^b	6.3 ^b	0.2 ^b	45.8	-	-	[98]	0.13
	Olive residues	74.8	12.8	5.1	7.3	50.95	5.28	-	38.63	-	-	[99]	0.11
	Alder wood	87.55	-	1.3	4.5	47.50	6.37	0.29	40.85	0.15	19.62	[100]	0.30
	paulownia wood	75.78 ^a	20.54 ^a	0.8 ^a	2.88 ^a	49.74 ^b	6.05 ^b	0.26 ^b	43.81 ^b	0.14 ^b	17.82 ^{LI}	[49]	0.12
Food production residues	Sugarcane bagasse	71.79 ^c	11.33 ^c	5.97 ^c	10.91 ^c	42.07 ^b	5.60 ^b	0.26	52.01	0.06	17.24 ^{HI}	[101]	-0.27
	Walnut shell	76.38	15.21 ^d	0.33	8.06 ^c	47.50	6.39	0.46	45.65	-	16.69 ^{HI}	[102]	0.15
	Peach stones	72.42	19.84 ^d	0.86	6.88	49.28	6.65	0.34	43.73	-	18.38 ^{GI}	[92]	0.27
	Groundnut shell	68.7	21.0	10.3	-	41.0	6.3	1.0	41.2	0.2	-	[103]	0.27
	Bagasse	74.5	19.5	6.0	-	36.3	5.8	0.3	51.5	0	-	[103]	-0.23
	Rice husk	51.4	12.1	36.5	-	36.0	4.8	1.2	22.3	0.2	-	[103]	0.58
	Waste newspaper	72.8	9.5	11.2	6.5	39.78 ^c	5.50 ^c	0.10 ^c	54.62 ^c	-	14.57	[69]	-0.41
Municipal organic waste	Year waste	72.1	17.7	10.2	5	52.50	6.83	1.28	39.3	-	-	[62]	0.38
	Food waste	70.7	18.5	10.8	4.4	51.68	6.21	1.14	40.97	-	-	[62]	0.20
	Potato	77.04 ^a	15.70 ^a	3.02 ^a	4.24 ^a	44.48 ^b	6.56 ^b	1.82 ^b	46.49 ^b	0.65 ^b	-	[70]	0.09
	Orange peel	76.49 ^a	20.60 ^a	2.91 ^a	-	47.32 ^a	5.75 ^a	1.39 ^a	42.45 ^a	0.18 ^a	18.47 ^{HI}	[104]	0.03
	Rice	84.42 ^a	15.18 ^a	0.40 ^a	-	45.79 ^a	6.32 ^a	1.68 ^a	45.56 ^a	0.25 ^a	18.14 ^{HI}	[104]	0.07
Industry organic by-product	Tissue paper	90.47 ^a	9.01 ^a	0.52 ^a	-	44.95 ^a	6.10 ^a	0.25 ^a	48.07 ^a	0.11 ^a	17.25 ^{HI}	[104]	0.01
	wool	84.76	14.00 ^a	1.24 ^a	-	59.33 ^a	4.19 ^a	2.62 ^a	31.09 ^a	1.53 ^a	20.92 ^{HI}	[104]	-0.07
	Rubber seed shell	80.98 ^a	6.62 ^a	3.81 ^a	8.59 ^a	44.31 ^b	4.38 ^b	0.51 ^b	50.67	0.13 ^b	-	[105]	-0.56
	Black-liquor lignin	69.01	25.77	1.58	3.65	63.42	5.83	0.81	29.94	-	-	[87]	0.36
Energy corps	Macroalgae	53.45 ^a	8.40 ^a	25.24 ^a	12.91 ^a	32.71 ^b	5.38 ^b	4.85 ^b	51.85 ^b	2.01 ^b	15.47 ^{LI}	[75]	-0.83
	Switchgrass	-	-	2.63	2.6	46.55	5.75	0.48	42.02	-	-	[106]	0.10
	Cellulose	93.75	6.19 ^d	0.06	-	42.23	6.36	0.03	51.34	0.03	-	[107]	-0.02
Neat cellulose, hemicellulose and lignin	Cellulose	94.35	5.65	0	-	39.95	6.20	0	52.77	1.08	-	[108]	-0.14
	Hemicellulose	74.54 ^a	18.34 ^a	2.00 ^a	5.12 ^a	39.18 ^b	6.32 ^b	0	54.50	0.01	-	[82]	-0.15
	Lignin	-	-	-	-	44.56	6.12	-	49.32	-	-	[109]	-0.01
		69.01	25.77	1.58	3.65	63.42	5.83	0.81	29.94	-	-	[87]	0.36
		62.90	32.60	2.70	1.80	62.45	5.68	0.56	30.61	0.70	-	[110]	0.32

[Proximate analysis] V: volatile; A: ash; FC: fixed carbon; M: moisture.

[Elemental analysis] C: carbon; H: hydrogen; O: oxygen; N: nitrogen; S: sulfur; Cl: chlorine.

[Heating value] ^{HI}: higher heating value; ^{LI}: lower heating value; ^{GI}: gross heating value.

^a: dry basis; ^b: dry ash free basis; ^c: received; ^d: by difference; ^e: calculated; -: not reported; ^m: moisture-free base.

Solid organic biomass presented in Table 3 has lower volatile matter, hydrogen and heat content, but higher ash and oxygen content compared to plastic waste. Feedstocks with a low H/C_{eff} ratio tend to produce more coke, which is not only harmful to the environment, but also hinders oil production during pyrolysis [54]. Gas chromatography/mass spectrometry (Py-GC/MS) studies using noble metal catalysts (W2C/AC, W2N/AC, Mo2C/AC and Mo2N/AC) have shown that mixtures with a H/C_{eff} ratio > 1.0

resulted in relatively high yields of aromatics, the rate is high [59]. The co-pyrolysis of solid biomass and plastic can increase the H/Ceff ratio and effectively improve the quality of pyrolysis oil.

Lignocellulosic biomass is one of the most abundant types of biomass resources on Earth, from sources such as forestry and agricultural residues, yielding over 100 billion metric tons per year [111]. Of these, only about 370 to 5100 million metric tons (approximately) of agricultural residues are treated each year [112-114]. Current estimates of the potential for converting forest residues into bioenergy are zero.

8 to 10.6 EJ per year by 2050 [115]. The efficient use of forest residues has become a viable option, especially in EU countries, where forest biomass generates more than half of the renewable energy sources [115]. Figure 4 shows that cellulose, hemicellulose and lignin are the three main components distributed unevenly in the cell wall, respectively skeleton, binding material and hard solids, while small amounts of extractables and ashes may also be present [116]. Cellulose is a linear macromolecular polysaccharide with a monomeric composition of $(C_6H_{10}O_5)_n$, where $n = 500-4000$, and long chains connected by β -1,4-glycosidic bonds [116].

The average composition of hemicelluloses (mainly xylans) can be expressed as $(C_5H_8O_4)_n$, where $n=50-200$. Hemicelluloses are heterogeneous branched, amorphous and random polysaccharides of pentoses (xylose and arabinose), hexoses (mannose, glucose, galactose and rhamnose) and acetylated sugars [117]. Lignin is a mononuclear aromatic polymer with a high degree of branching and substitution. It is commonly found as lignocellulosic complexes and is often associated with adjacent fibers of cellulose and hemicellulose [118]. Thermal analysis of these materials showed that pyrolysis of hemicellulose and cellulose occurred at 220–315°C and 315–400°C, respectively.

However, lignin is more thermoelastic, causing weight loss over a wide temperature range from 160 to 900°C [119].

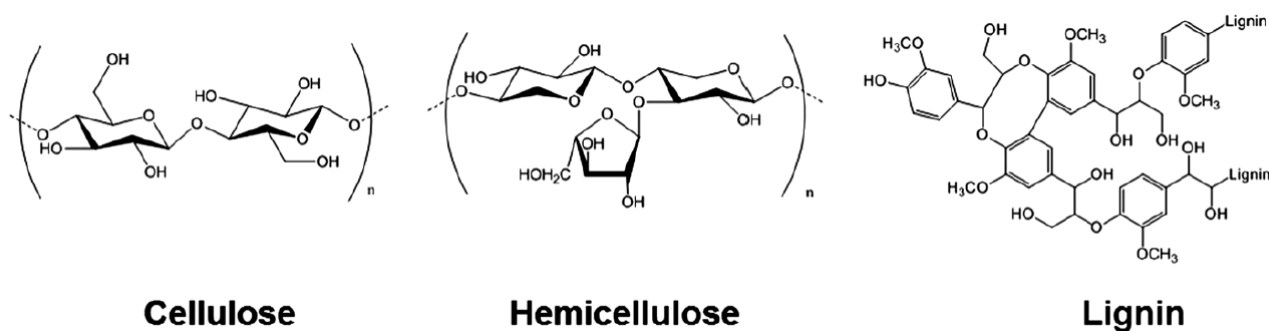


Fig. 4. Major components of lignocellulosic biomass [21].

2.3 Calculation of synergistic effects

Synergistic effects can be defined as binary, ternary or multi-component mixtures of biomass and plastics producing effects greater or less than those calculated or determined based on the weighted values of the individual loads in the co-cracking process. Changing the feed mixing ratio is one of the most important factors affecting the synergistic effect [43,45,85].

In order to determine the presence of synergistic effects in the co-pyrolysis of mixtures of plastic and biomass, the indices obtained from the experimental and calculated values can be compared. Theoretical values can be calculated from the scale-weighted average of the individual pyrolysis measurements [105]. Therefore, a positive synergistic effect (ΔY) occurs during co-pyrolysis if the experimental value is greater than the weighted total calculated value [69]. For example:

$$Y_{\text{Calculated}} = a \times Y_{\text{Biomass}} + (1-a) \times Y_{\text{Plastic}} \quad (2) \quad \Delta = * 100\% \quad (3)$$

Among them, $Y_{\text{Experimental}}$ is the experimental value of the co-pyrolysis mixture, and the the yield of the product can be (Weight 33

(kg), volume (m) or conversion rate (%), etc.), $Y_{\text{Calculated}}$ is the average calculated value by weight (kg, m or % 3, etc.); Y_{Biomass} is the pyrolysis experiment of a single biomass value (kg, m or % etc.); Y_{Plastic} is the 3

individual experimental value of the plastic in pyrolysis (kg, m or % etc.)

), a is the percentage of plastic mixture (% by weight). ΔY is called the degree of synergistic efficiency in the co-pyrolysis process and is usually expressed as a percentage.

3. Challenges and Opportunities

With increasing attention to waste management, co-pyrolysis of waste plastics and solid biomass has been investigated to enhance synergistic effects, reduce activation energy or fuel consumption. energy, increase product yield, select, mitigate or reduce Product processing avoids the release of toxins. As far as we know, there are still many challenges ahead that require our attention and resolution. These problems present many opportunities for researchers and engineers. Specifically, challenges and opportunities exist in:

(1) Co-pyrolysis of multicomponent mixtures of plastic waste solid biomass should be considered as raw materials in future studies, as current studies are limited to binary mixtures. However, in the practical application of the co-pyrolysis technology, it is difficult to separate a single plastic waste a single solid biomass from the waste and then mix the selected raw materials together to match the optimum conditions to obtain the co-desired pyrolysis. Pyrolysis results. get.- Pyrolysis. Therefore, multicomponent feedstocks that approximate real waste mixtures should be further investigated.

(2) Colysis scale studied for scaling performance and scaling studies. At present, the research on the co-pyrolysis of waste plastics and solid biomass has been studied from two aspects of mechanism and yield. However, most surveys are conducted at the gram level or below. It is necessary to increase the large-scale research, and to complete the industrial production and market application of substitute liquid oil by co-pyrolysis is an important goal in the future. Potential alternative liquid oils for diesel, gasoline, and boiler fuels as co-pyrolysis oils have not been sufficiently researched to investigate their use. Based on the life cycle analysis, the selected efficient and economically feasible methods should be expanded and optimized as appropriate to meet market demands and reduce pollution from waste disposal and fuel combustion fossils. The amount of plastic waste and solid biomass that exists in the world, the amount of resources will not be an obstacle. Equally important is the research of technologies for the collection, transport and storage of raw materials, as well as the improvement of co-pyrolysis technologies at the same time. Downstream processing of recycled materials and value-added products is also important.

(3) The co-pyrolysis process must take into account the self-heating path. This review shows that the heat input resource of co-pyrolysis is still dominated by electric power, which must be replaced by low-quality power before the co-pyrolysis technology can be used on a large scale. Combustion of the produced gases, oils and solid residues from the co-pyrolysis system provides heat that can be used for energy recovery

and waste management. The self-heating route in the co-pyrolysis process can cover a large part of its own energy demand instead of electricity supply, which will make the co-pyrolysis technology more economical and competitive on the energy supply market.

(4) Although co-pyrolysis of waste plastics and solid biomass on zeolite-based catalysts has been studied differently, transition metal-based catalysts suffer from short lifetime, low carbon efficiency and high coking in the process. This remains a major challenge. The improvement of catalysis must take into account the synergistic effects between plastics and biomass. The pyrolysis properties of plastics and biomass must also be taken into account to obtain an optimal catalyst for the co-pyrolysis process. Currently, high-value catalysts

such as ZSM-5 are not suitable to operate in the harsh environment of in situ catalytic pyrolysis because coking and deactivation rapidly reduce their activity and simultaneously reduce their selectivity. Therefore, for future catalytic co-pyrolysis studies, these catalysts should be limited to ex situ incorporation to provide high quality products and minimize deactivation. Catalysts with higher tolerance and applicability in harsh environments should continue to be developed in the future. Catalysts suitable for this research will involve the use of low-value materials and the development of carbonaceous materials,

such as activated carbons that have been modified to increase thermal and oxidative stability. However, due to the imminent need for their development and our lack of in-depth understanding of co-pyrolysis and its complex reaction regimes, we conclude

that this route is difficult and less attractive. Simultaneous product improvement via ex situ catalysts versus developing non-catalytic co-pyrolysis with optimal process performance. This alternative, involving ex situ catalysis, is more efficient and preferred because it can be used with existing catalysts and can continue to operate for longer.

As mechanistic knowledge of co-pyrolysis and interactions grows, future research may involve improving the selectivity of desired value-added chemicals.

(5) Improve the level of separation and purification of co-pyrolysis chemicals with high added value. The liquid compounds produced by co-pyrolysis are more complex than those produced by the pyrolysis of plastic waste or solid biomass. Although hundreds of chemical constituents have been detected in co-pyrolysis liquids, there is a lack of research efforts to harvest chemicals from oils or co-pyrolysis liquids to produce products of great value for important applications such as the medical and food industries.

8. Conclusion

This article reviews the co-pyrolysis of plastic waste and solid biomass. Focusing on the production of alternative fuels and value-added products, the development of co-pyrolysis of waste plastics and solid biomass is essential as it can provide synergistic solutions for waste management, climate change mitigation, climate change and environmental protection. Co-pyrolysis enables efficient waste management and waste carbon utilization, providing a loop in the fate of fossil fuels and energy used in waste generation while minimizing unsustainable pathways such as landfills and incineration, and reducing marine pollution to keep the environment to a minimum. Toxic emissions from plastic waste and mitigation incinerators.

Review articles report the thermochemical properties of typical plastic waste and solid biomass. Calculate the effective hydrogen to carbon ratio for various plastic wastes and solid biomass according to the revised benchmark. Co-pyrolysis was examined from the perspective of major plastics (PET, HDPE, PVC, LDPE, PP, PS, etc.) and typical solid biomass, and the synergistic effects and influencing factors among the materials first have been summarized. Overall, HDPE, LDPE, and PP had a positive synergistic effect on liquid yield when co-pyrolyzed with solid biomass, while PET, PS, and PVC had a positive synergy on the solid or gas yield. Co-pyrolysis methods and operating conditions for TGAs, pyrolyzers, fixed bed reactors, fluidized bed reactors, microwave reactors and multi-stage pathways, as well as TG, MS, FTIR and their combinations are discussed in detail. ZSM-5 catalysts, transition metal catalysts, multi-catalysts and ex-situ catalytic co-pyrolysis (CCP) are reviewed, focusing on the catalytic effect with due consideration of the plastic/biomass ratio, raw material/catalyst ratio, pyrolysis temperature, methods and main factors of manufactured products. Overall, PCC of waste plastics and solid biomass offers a promising technology that can significantly reduce energy input and improve selectivity towards liquid and chemical materials. Oils and liquid chemicals, gases and solid residues from co-pyrolysis are reviewed in terms of yield, composition and special properties. Finally, challenges and opportunities for the future development of co-pyrolysis are discussed.

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