

Applications of pyrolysis for carbonaceous wastes in solid waste management – A mini-review

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ABSTRACT

Due to the aggravating problem of solid waste disposal and rising demand of fuels for energy generation, pyrolysis can serve as a promising solution to both these challenges. The majority of the municipal solid wastes are constituted of carbonaceous wastes including biomass. Pyrolysis can be universally applied to all these types of wastes to obtain non-condensable fuel gases, pyrolysis oils and solid coke achieving complete waste disposal. In the present study, a review of pyrolysis with respect to various types of waste feedstock is presented. The interactions of the various types of waste feeds during co-pyrolysis were also reviewed. The applications of the products obtained as well as their further upgrading is also discussed. The presence of catalyst, reaction conditions, heating rate as well as the type of reactor, influence the yield as well as the composition of the products to a great extent. Pyrolysis of single feed as well as co-pyrolysis is also reviewed. Some co-pyrolysis studies reported better results than single feed pyrolysis owing to the synergistic interactions between waste feeds. This paper provides an overall outlook of the current scenario of the pyrolysis techniques for solid waste management.

KEYWORDS

Pyrolysis, Co-Pyrolysis, Solid Waste Management, Pyrolysis oil, Non-Volatile gases, Char.

INTRODUCTION

The challenges in ever-increasing amount of solid wastes has brought about noteworthy research in solid waste management.

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Depending on nature and source of wastes, they can be classified as medical, industrial, agricultural, municipal, vehicular waste, etc. Currently, the major disposal techniques for waste management are: a) landfilling b) composting c) sewage treatment d) incineration and e) recycling (Rushton 2003). Out of these, recycling of wastes is restricted to only reusable wastes, while composting is restricted to biodegradable solid wastes and sewage treatment to sewage sludge. These methods require proper segregation of waste feedstock before disposal implementation. Majority of wastes are preferably landfilled due to its cheap and simple nature (Arsova et al. 2008). However, landfilling requires a huge land which leads to strain on land resources (Omar and Rohani 2015). The leaching out of heavily polluted leachates and emission of landfill gases from landfills has led to many harmful consequences on environment and people residing nearby (Bernard et al. 1996; Crowley et al. 2003; El-Fadel et al. 1997; Vrijheid 2000). The leachates are a mixture of high concentration organic and inorganic contaminants including heavy metals and are highly toxic due to their synergistic or antagonistic effects and different physical-chemical properties of contaminants (Cameron and Koch 1980; Kjeldsen et al. 2002; Marttinen et al. 2002; Wiszniowski et al. 2006). Incineration allows better mass and volume reduction of wastes and good energy recovery and seems to be a better option than landfilling (Roy et al. 2011). However, the fly ash emissions released during incineration are hazardous due to high content of chlorides and fluorides, sulfur and nitrogen compounds, heavy metals like mercury and organic compounds. Some deadly side-effects on human beings reported are congenital abnormalities, birth weight, twinning, still births, sex ratios, infant death, facial clefts, urinary tract defects, neural tube and heart defects (Ashworth et al. 2014; Margallo et al. 2015; van Velzen et al. 2002; Williams 1990). Sometimes greater amount of fuel is required to be supplied to ensure adequate combustion temperatures,

making the incineration process less energy efficient (Ji et al. 2016; Yang et al. 2006).

Pyrolysis is a thermal degradation process of heating in absence of oxygen or air to produce gaseous components, tar and pyrolysis char residues (Ahmed and Gupta 2009). The pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis (Demirbas and Arin 2002). Due to 'carbon negative' energy approach, pyrolysis deserves serious research and development worldwide for energy and controlling global warming (Lee et al. 2010). The liquid and gaseous fractions obtained are a valuable fuel source; while the solid fraction (char) has the potential of low grade carbon black or as carbon adsorbent (Lee et al. 2015; Martínez et al. 2013; Mohan et al. 2006b; Phan et al. 2008). Pyrolysis of waste also produces products that can be used as chemicals and high performance materials (carbon fibers and ceramics) other than fuels (Blazsó 1997). During recent years, pyrolysis has undergone an important evolution from a promising scientific idea to an alternative that is very close to reality with commercial opportunities (Aguado et al. 2008). Although the pyrolysis oils cannot be directly used as engine ready fuel but the fuel quality and contamination issues can be resolved by fuel additives and fuel finishing operations in terms of physical, catalytic and chemical upgrading (Butler et al. 2011a; Isahak et al. 2012).

Presently, fast pyrolysis of biomass is deemed as robust alternate technology for the paradigm shift from current crude oil fuel platform to a sustainable, more flexible fuel platform (Butler et al. 2011b). Based on ways of energy transfer, microwave assisted pyrolysis has an advantage of providing rapid and energy-efficient heating compared to conventional technologies, and thus facilitating increased production rates (Jones et al. 2002; Lam and Chase 2012). Hence pyrolysis can be a promising technique for waste management.

Literature has reported several significant reviews on the development of the pyrolysis process. Blazsó (1997) has reviewed the studies on the thermal decomposition mechanisms of polyolefines, polystyrenes, acrylic polymers,

polyesters, polyethers, formaldehyde resins, polyamides, sulfur and silicon containing polymers. Aguado et al. (2008) have reviewed in detail the thermal and catalytic processes for recycling of plastics and several commercial processes for the preparation of diesel fuel. Butler et al. (2011a) has studied the state of art of commercial pyrolysis processes for the production of liquid transport fuels from waste polyolefins (polyethylenes and polypropylenes). Bulushev and Ross (2011) have reviewed chemistry of various catalytic processes for production and upgrading of the pyrolysis oils obtained from biomass pyrolysis. White et al. (2011) have reviewed the kinetic models and mathematical approximations currently employed in solid state thermal analysis and isoconversional model-fitting methods for estimating the related kinetic parameters. Isahak et al. (2012) have presented an updated review of biomass pyrolysis focusing on the characterization of feedstock, reactor design, product formation and physical, catalytic and chemical upgrading of the products. Jahirul et al. (2012) have discussed the status of biomass pyrolysis technology and its potential for commercial applications to produce bio-fuel in light of pyrolysis principles, biomass sources and characteristics, types of pyrolysis, reactor design, products and the economics of bio-fuel production. Mohan et al. (2006a) have reviewed in detail the pyrolysis of wood biomass and the characteristics of bio-oil produced. Butler et al. (2011b) have reviewed the laboratory work and developments on fast pyrolysis and upgrading techniques for its commercialization. Fonts et al. (2012) have reviewed the state of art of the sewage sludge pyrolysis for liquid production, focusing on the various factors influencing the process and chemical and physical properties of the pyrolysis oil obtained. Yang et al. (2013) have reviewed the pyrolysis of the waste electronic and electric plastic wastes and the dehalogenation of the pyrolysis oils.

A review based on the study of feedstock of pyrolysis and their interaction during co-pyrolysis has not been reported yet. The aim of this review is to study pyrolysis and co-pyrolysis focusing on the properties, composition and nature of waste feeds and their effect on the interactions during co-pyrolysis for solid waste

management. The effect of the reaction conditions such as temperature, heating rate, presence of carrier gas, nature of catalyst on the yield and physicochemical properties of products are also discussed. The potential of pyrolysis products to serve as a source of high quality fuels and chemicals is also discussed. The review provides an outlook of waste pyrolysis from the aspect of feedstock, particularly required for an insight for waste-to-energy processes. The nature of interaction of the different feeds with each other and their effect on the yield and composition of the products during co-pyrolysis studied in this review provides a novel aspect in environmental engineering. Similar work has been reported previously by Sannita et al. (2012), but their study is restricted to triglyceride-based materials, wood and compounds derived from wood and few hydrocarbon and oxygenated polymers. This review includes pyrolysis of carbonaceous wastes including paper wastes.

1 Single Feed Pyrolysis

1.1 Biomass

Pyrolysis is a promising and environment friendly way of energy recovery from biomass as biomass is the only renewable source of fixed carbon (Bridgwater and Bridge 1991; Serrano-Ruiz and Dumesic 2011; Zhong et al. 2010). Considerable work has been reported to study the potential of agricultural wastes as a source of biofuels. Pyrolysis of rice husks (Meesuk et al. 2012; Williams and Nugranad 2000; Worasuwanarak et al. 2007), pine biomass (Aho et al. 2007), chlorella algae (Babich et al. 2011), wheat straw and husks (Krishna et al. 2015), beech wood (Stephanidis et al. 2011), combed cotton wastes (Barışçı and Öncel 2014), guayule (Boateng et al. 2016), douglas fir, para rubber seed (Chaiya and Reubroycharoen 2013), white ash, switchgrass, corn stover (Chen et al. 2016c), olive cake (Gerçel and Gerçel 2007), miscanthus, douglas fir and oak (Le Brech et al. 2015), cassava plant residues (Pattiya 2011), mangaba seed (Santos et al. 2015), rapeseed cake (Smets et al. 2011), posidonia oceanica, lacustrine alga and white-pine (Chiodo et al. 2016), corn cob (Yu et al. 2010), tobacco wastes (Wu et al. 2015b) has been reported.

The yield and chemical composition of the products is influenced by a variety of factors

such as temperature, presence of catalyst, size of the feed particles, etc. (Chaiya and Reubroycharoen 2013; Chen et al. 2016a; Demirbas 2010; Krishna et al. 2015). Various ways for upgrading the quality of the products, especially for use of pyrolysis oil as fuel have been reported.

One of the important products obtained during pyrolysis of the materials is bio-char. It possesses high calorific value and relatively low ash content making it suitable as a good solid fuel (Gil et al. 2012). Some other value-added products are also obtained. A high percentage of silica (88%) was recovered from overall valorization of the bio-char of rice husk flash pyrolysis (Alvarez et al. 2014). Potassium silicate of electronic grade can be obtained from bio-char more easily than from fusion of sand along with a good quality activated carbon as a by-product (Jain et al. 1994). The char could be used as an additive material or good solid fuel with binders and additives due to its high energy content (Barışçı and Öncel 2014; Maiti et al. 2006). Due to good absorbing properties, bio-char also finds its uses as adsorbent. The char obtained at high temperatures is highly porous with effective tar removal capacity (Paethanom and Yoshikawa 2012). Increase in the pyrolysis temperature increases the carbon content in biochar and gases (Chen et al. 2016c). The char is mainly aromatic polymer of carbon atoms (Hu et al. 2008). Li et al. (2015a) have reported an increase in energy and char yield due to the effect of $\text{NH}_4\text{H}_2\text{PO}_4$ on rice husk pyrolysis. Uzunov et al. (2012) have carried out fixed bed slow pyrolysis of rice husks for determining the effect of pyrolysis temperature on the properties of solid residues. Carbon black of high specific surface area and pore volume can be synthesized from rice husk by hydrolysis, carbonization and pyrolysis (Wang et al. 2011). Wu et al. (2015a) have suggested that the bio-char from microwave pyrolysis is more uniform with less secondary bio-char which are produced from secondary reactions of volatiles.

Generally, the yield of non-condensable gases increases with increase in the temperature, lower heating rate and longer residence time (Khor et al. 2010). The yield also depends on the conditions, types of biomass and presence of

catalyst (Buzetzi et al. 2012; Xie et al. 2015). Homma et al. (2013) have developed a new pyrolysis technology for wood pyrolysis that has a low manufacturing cost and less maintenance. It was quite feasible in rural areas and the gases obtained could be directly used in gas engine generator. The gases from rice husk pyrolysis can also be used in auto thermal pyrolysis process if the moisture content is controlled (Park et al. 2014). The gases obtained could be further reformed for the production of hydrogen gas (Uddin et al. 2014). Demirbaş (2005) has reported an increase in hydrogen production from agricultural residues via pyrolysis with an increase in temperature. The introduction of steam into the reactor system can drastically increase the hydrogen production (Adebanjo et al. 2007). The yield of methane and hydrogen gases and heating value of the gases can be also increased by torrefaction pretreatment (Chen et al. 2015). The process of mild pyrolysis in the temperature range 200-350°C which leads to removal of water and volatiles through decomposition of hemicellulose in wood, is termed as torrefaction (Kolokolova et al. 2013). Zhang et al. (2015d) have reported the combined water washing-torrefaction pretreatment for effective removal of inorganics. The bio-char was obtained with huge surface area and had the potential to be used as soil amendments.

The most important component obtained during pyrolysis is pyrolysis oil. Oil contains alkanes, alcohols, hydroxybenzenes, alkoxybenzenes, dioxolanes, aldehydes, ketones, carboxylic acids, esters, nitrogen-containing organic compounds (Lu et al. 2012). Due to its potential to be used as fuel, it can replace diesel and gas for on-site power generation and heating in furnaces, boilers, gas turbines etc. (Barth and Kleinert 2008; Zheng and Kong 2010) Literature has reported several methods to increase the quality and yield of pyrolysis oil. Bok et al. (2014) have designed a tilted-slide fast pyrolyzer with spray type condenser for the large-scale production of biocrude-oil from douglas fir in which the bio-oil from first and fourth condensers could be directly applied to conventional combustors. Kunkes et al. (2008) have reported the catalytic pyrolysis of biomass based on the integration of several flow reactors operated in cascade mode,

where the effluent from the one reactor is fed to the next reactor and the first flow reactor contained monofunctional compounds, such as alcohols, ketones, carboxylic acids and heterocycles that could also be used to provide reactive intermediates for fine chemicals and polymers markets. Heo et al. (2010) have reported pyrolysis of rice husk in fluidized bed reactor in which the bio-oil production was most effective when the fluidizing medium was the product gas itself. Thangalazhy-Gopakumar et al. (2011) have reported large reduction in high molecular weight, oxygenated compounds in the pyrolysis oil when the carrier gas was changed from helium to hydrogen during pyrolysis. Williams and Besler (1993) have reported the pyrolysis study of rice husk in thermogravimetric analyzer and static batch reactor wherein water, CO and CO₂ were evolved in lower temperature regime of decomposition and oil, water, hydrogen, hydrocarbon gases and lower concentrations of CO and CO₂ were evolved in higher temperature regime. Le Brech et al. (2015) have reported the pyrolysis in U-shaped fixed bed reactor which allowed external mass transfer control, bed temperature control and char quenching at targeted temperatures. Undri et al. (2014b) have reported microwave assisted pyrolysis of corn derived plastic bags which can avoid the anaerobic digestion of these bags without any energy recovery. Gerçel and Gerçel (2007) have pyrolysed olive cake and found that at optimum conditions, the calorific value of pyrolysis oil is very close to those of petroleum fractions. Santos et al. (2015) have reported that the bio-oil from mangaba seed was promising as fuel after upgradation due to the presence of long chain acids. Demirbas (2009) have pyrolysed olive husk, hazelnut shell, spruce wood, and beech wood samples and reported that the density of bio-oil was 1,170–1,230 kg/m³, compared to 800-1000kg/m³ of heavy petroleum oil.

Guha et al. (1987) have studied the potential use of pyrolysis oil in germicide manufacture due to the presence of toxic phenolic compounds. Ji-Lu (2007) has conducted pyrolysis of rice husk and reported that the bio-oil can be directly used in boiler or furnace without further upgrading and the cost of pyrolysis can be greatly reduced by

using charcoal combustion for heating and hot flue gas as carrier gas. Torri et al. (2016) have reported an increase in the percentage of aromatic hydrocarbons in bio-oil during catalytic fast pyrolysis of softwood, thus indicating its potential as liquid fuel. Lu et al. (2011) have proposed low temperature fast pyrolysis of biomass impregnated with zinc chloride to obtain furfural from bio-oil while acetic acid was obtained as by-product. The addition of methanol stabilized the bio-oil and enhanced the quality by decreasing viscosity and ageing rates of bio-oil (Lu et al. 2008). Li et al. (2012) have seen an increase in the yield of water soluble organics and heating value with decrease in acetic acid content and ring opening reactions of cellulose during fast pyrolysis of rice husk with mineral bed materials. Qian et al. (2014) have reported the facilitation of dehydration and decarboxylation of higher calorific value bio-oil under elevated pressure in the pyrolysis of rice husk. Banks et al. (2014) have reported that during pyrolysis of *Miscanthus* pretreated with Triton X-100 surfactant, the best quality organic oil was produced with highest concentration of Triton X-100 surfactant. Shen et al. (2015) have reviewed the opportunities of the fast pyrolysis products as value added chemicals and fuels. Damartzis and Zabaniotou (2011) have discussed the emerging challenges and opportunities of the applications of process integration on chemical conversion of biomass to second generation liquid biofuels.

Chen et al. (2011) have reported a decrease in the total bio-oil content, higher water content, higher pH, and lower alkali metal content in the bio-oil when the hot vapor filtration of bio-oil was conducted. It was also reported that the PAH content increased when the temperature increased and around 800°C charcoal liquid was produced (Zhai et al. 2015). Catalysis is one of the assuring approaches for upgrading the bio-oil. The use of catalyst decreased the bio-oil yield, but enhanced the small molecular compound yield and decreased the amount of oxygenated groups in bio-oils (Bridgwater 1996; Zhou et al. 2013). The pyrolysis oil before catalysis was homogeneous, of low viscosity and highly oxygenated with presence of polycyclic aromatic hydrocarbon (PAH) in low

concentration (Williams and Nugranad 2000). Aho et al. (2007) have reported the formation of less organic oil and more water and PAH on the catalytic pyrolysis of pine biomass with zeolites of stronger acidity. Antonakou et al. (2006) have proposed the use of mesoporous catalysts Fe–Al-MCM-41 and Cu–Al-MCM-41 as best metal containing catalyst for phenol production from bio-oil. The phenol concentration can be further increased by upgrading of the bio-oil obtained from hydrothermally pretreated biomass (Stephanidis et al. 2011). Phenol could be further used in adhesive industry (Effendi et al. 2008). Wang et al. (2010) have reported an increased yield of gaseous and char products with use of K_2CO_3 as a stronger catalyst for decomposition of hemicellulose, cellulose and lignin constituents. Various pretreatment techniques and product upgrading via catalysis also facilitate increase in the quality of the bio-oil. Bridgwater and Bridge (1991); French and Czernik (2010), Galadima and Muraza (2015) have studied the catalytic upgrading of the primary fast pyrolysis products for removing oxygen from organic compounds to give aromatics and other hydrocarbon products. The products can be further converted into gasoline and diesel and the condensed liquid can be hydrotreated to a naphtha like product also for up gradation into transport fuels (Kim et al. 2013).

The hydroprocessing increases the intrinsic hydrogen content of the pyrolysis oil, producing polyols and alcohols. The zeolite catalyst then converts these hydrogenated products into light olefins and aromatic hydrocarbons as much as three times higher than that produced with the pure pyrolysis oil (Vispute et al. 2010). Babich et al. (2011) had pretreated *Chlorella* algae with Na_2CO_3 and the decomposition temperature shifted to lower value, yield of gas increased and yield of liquid decreased. Barışçi and Öncel (2014) have reported that bio-char from pyrolysis of combed cotton wastes in a fixed bed reactor with Na_2CO_3 and $CaCO_3$ as catalyst can be used as additive material or fuel due to its high energy potential. Meesuk et al. (2012) have further reported that the quality of the bio-oil can be further improved to a level suitable for a potential liquid fuel and chemical feedstock by hydrolysis of rice husk using Ni/LY char at

high temperature and the pyrolysis oil contained less acids, higher aromatics and showed higher heating value leading to 40% energy recovery in bio-oil. Zhang et al. (2015a) have studied the microwave assisted catalytic fast pyrolysis of biomass using HZSM-5 catalyst and reported that the relative contents of the aliphatic hydrocarbons, aromatic hydrocarbons and oxygen-containing aromatic compounds first increased and then decreased, whereas the relative content of oxygen-containing aliphatic compounds first decreased and then increased.

1.2 Paper wastes

Paper industry generates a significant amount of wastes and the waste composition depends on the type of paper produced and the origin of cellulose fibres. (Méndez et al. 2009). Nearly 11 million tons of paper wastes are generated per year by European pulp and paper industry, of which 70% originated from the production of deinked recycled paper. The paper and pulp production from virgin pulp generates less wastes with less organics than deinked pulp (Monte et al. 2009). Paper mill sludge contain massive heavy metal, pathogen and parasites making it very easy to corrupt and produce odor causing secondary pollution to the environment and threat to human beings and animals (Liu et al. 2010). Therefore one of the most important tasks for environmental protection is the safe disposal of sludge from paper and pulp industry (Yu et al. 2002).

The four main compounds in bio-oil obtained from waste paper pyrolysis are anhydrosugar, carboxyl compounds, carbonyl compounds and aromatic compounds (Li et al. 2005). The gases generated during pyrolysis of newspaper wastes are composed of H₂, CO, CO₂, and CH₄ with a trace amount of C₂H₄ and C₂H₆ and the production of hydrogen rich gaseous fuel is favored at higher temperature and higher retention time (Bhuiyan et al. 2009). It was also reported that there is an increase in the yield of liquid and gaseous products with an increase in the solid waste pyrolysis temperature (Demirbaş 2002), and char yield increases with an increase in the heating rate (Gupta et al. 1999). The performance of fast pyrolysis for energy transfer from paper waste sludge to liquid and solid products is considerable higher than vacuum

and slow pyrolysis due to higher yield of condensable organic compounds and less water content (Ridout et al. 2016). Fast pyrolysis is quite promising due to low optimal reactor temperatures and high bio-oil yield. The non-condensable gas yield increases due to promotion of exothermic reaction for high heating rates (Ridout et al. 2015). Biswal et al. (2013) have pyrolysed paper cup waste in a stainless steel semibatch reactor and found that the pyrolytic liquid contains around 18 types of compounds having carbon chain length in the range of C₆ – C₂₀, and can be used as valuable chemical feedstock. Jiang and Ma (2011) have reported that microwave pyrolysis of paper mill sludge was best performed when 5% NaOH was added as microwave absorber in CO₂ atmosphere. Reckamp et al. (2014) have subjected paper mill sludge to a combination of acid hydrolysis and torrefaction pretreatment and found that the bio-char yield was higher and ideal to be used as soil amendment agent or sorbent material. Mendez et al. (2014) have reported the use of bio-char from deinking paper sludge pyrolysis to treat nickel polluted soil.

Calisto et al. (2014) have reported production of adsorbents obtained in the pyrolysis of paper mill sludge for the removal of highly consumed antidepressant (citalopram) from water. Devi and Saroha (2015) have studied the PAH toxicity and sorption behavior of bio-char obtained in the pyrolysis of paper mill effluent treatment plant and reported that the concentration of PAHs in bio-char were within the permissible limits prescribed by US EPA. Strezov and Evans (2009) have reported that a large fraction of mineral matter (56%) in the charcoal produced by pyrolysis of dry paper sludge and also found that the energy from bio-gas can utilized to recover the heat required for pyrolysis thus reducing the external heat supply requirement. Zhang et al. (2015g) have reported low temperature microwave assisted pyrolysis of paper deinking residue for simultaneously efficient fast recovery and separation of organic and inorganic content in which the organic fraction of bio-oil generated was a potential source of valuable aromatic compounds. Zhang et al. (2015f) have further reported the low temperature microwave assisted fast pyrolysis

of waste office papers (printed or photocopied) and the application of bio-oil as adhesive for aluminum-aluminum bonding.

2. Co-pyrolysis of carbonaceous mixed feeds

2.1 Biomass with other feeds

The oil obtained from pyrolysis needs upgrading due to considerable amounts of oxygen in them making them unsuitable as a fuel due to low caloric value, corrosion problems, and instability. Generally upgrading is done by addition of a catalyst, solvent and large amount hydrogen, which make the process less cost efficient due to high costs of the additions (Abnisa and Daud 2014; Lee and Kim 2015). Therefore co-pyrolysis of wastes has gained importance due to the certain synergistic effects such as higher quantity and better quality of oil or limited supply of certain feedstock which thus improves the overall pyrolysis process (Oyedun et al. 2014; Sarkar and Chowdhury 2014). Liu et al. (2013) have reported the synergistic effects of the WEEEs and biomass occurring during the co-pyrolysis due to significantly higher yield of bio-oil than individual pyrolysis of components with no formation of polybrominated dibenzo-p-dioxins. Sajdak and Muzyka (2014) have reported a reduction in heat energy requirement during co-pyrolysis of plastics with biomass thus showing synergistic effects. Xue et al. (2015) have observed an increase in the production of furan, acids and water with improved higher heating value of the resulting char due to significant synergetic effects during co-pyrolysis of red oak and high-density polyethylene (HDPE). Wang et al. (2016c) have reported an increase in gas and liquid yields but a decrease in char yield due to the synergetic effect during the co-pyrolysis of sewage sludge and wheat straw which also accelerated the pyrolysis reactions. Zhang et al. (2015c) have reported significant promotion of aromatics due to synergistic effect between corn stalk and food waste thus making catalytic co-pyrolysis an efficient method for production of aromatics and other petrochemicals.

Several studies on the products of biomass co-pyrolysis have been done. Goldfarb and Ceylan (2015) have studied the sustainability of second generation fuels by pyrolysis of highly volatile bituminous Pennsylvanian coal blended at 90,

80, and 50 wt% with one of three biomasses: feed corn stover, brewer's spent grains or cocoa shells. Paradela et al. (2009) have performed slow batch co-pyrolysis using mixtures of plastics, tires and forestry biomass wastes and found that the plastic content in the mixture affects the product yield and composition greatly. Ro et al. (2014) have performed co-pyrolysis of swine manure with agricultural plastic waste and reported the potential of using pyrolysis technology to manage two prominent agricultural waste streams (spent plastic mulch films and swine solids) along with production of value-added biochar that could be used as a power source for local farm operations. Uzun and Yaman (2014) have reported the co-pyrolysis of scrap tire and *Juglans regia* shell as environmental friendly process for production of valuable chemicals and fuels from the wastes.

Alvarez et al. (2015) have studied the co-pyrolysis of the sewage sludge and lignocellulosic biomass in a conical spouted bed reactor and reported minimization of the gas production reactions from bio-oil (mainly promoted by the catalytic activity of the ash in the sludge). Zhang et al. (2014) have carried out co-pyrolysis of pine sawdust and plastics (polyethylene, polypropylene, and polystyrene) in a catalytic fluidized bed reactor in order to improve the yield of hydrocarbons (aromatics and olefins). Zhou et al. (2015a) have conducted co-pyrolysis of three municipal solid waste (MSW) components (rice, poplar wood and PVC) and reported an increase in the generation of CO₂ and CO at slower rate. Zhou et al. (2015c) have co-pyrolysed polyvinyl chloride (PVC) and biomass components (hemi-cellulose, cellulose and lignin) and have reported decrease in HCl and PAH yields and significant increase in tar yield. Onal et al. (2014) have carried out co-pyrolysis of almond shell as biomass and high-density polyethylene and found that the oils produced were having higher carbon (26% higher) and hydrogen content (78% higher), lower oxygen content (%86 less) with a higher heating value (38% higher) than those of biomass oil.

Further upgrading of the product can be done by catalytic co-pyrolysis. Jin and Wang (2015) have reported equal mean temperature of mass loss

of the pyrolysis oil of rice husk and waste tires in 1:1 ratio with SBA-15 catalyst and diesel, thus showing similar evaporation properties of pyrolysis oil and diesel. Pinto et al. (2013) have reported response surface methodology as a method for prediction of liquid yields from the pyrolysis of waste mixtures consisting of 10% of pine, 10% of scrap tyres and 80% recycled plastic as a suitable method for optimizing the experimental conditions that favor the formation of desired gaseous and liquid compounds. Yao et al. (2015) have reported ZSM-5 modification with P and P/Ni for improvement of catalyst's activity and life time for co-pyrolysis of biomass and plastics. Zhang et al. (2015b) have reported catalytic co-pyrolysis of corn stalk and high density polyethylene (HDPE) over HZSM-5 zeolite catalyst for promoting efficient production of aromatic hydrocarbons. Luo and Fu (2015) have reported the use of biomass tar for the production of directly reduced iron by co-pyrolysis of biomass tar and iron ore fines. Zhang et al. (2015e) have carried out co-pyrolysis of sewage sludge and biomass in a vacuum reactor and reported higher gas yield of the blend fuel than both the individual parent fuels thus approving the method feasible for fuel production. Zhang et al. (2011) have studied fraction distribution of heavy metals in co-pyrolysis of sewage sludge and corn straw and reported that the carbon residues obtained were nonhazardous and safe.

2.2 Coal and RDF with other feeds

Co-pyrolysis with coal is a good waste management option due to high energy obtained during pyrolysis as well as co-pyrolysis of the coal (Coimbra et al. 2015). The composition and quantity of products during these processes depend greatly on the coal type, pyrolysis temperature and heating method (Ding et al. 2015). The evolution of gases is increased by rising the temperature and longer residence time resulting into secondary cracking of tar and gaseous hydrocarbons (Reichel et al. 2015). During coal pyrolysis, there is a decrease in the differences in the nitrogen distribution in the char precursors to the extent that it cannot influence the formation of nitrogen oxides during combustion of chars significantly (Pels et al. 1995). The formation of NH_3 can be promoted by the presence of NaOH, KOH and $\text{Ca}(\text{OH})_2$

which however suppresses HCN formation (Ohtsuka et al. 1997). Similarly, sulfur containing gases are evolved during coal pyrolysis and co-pyrolysis (Calkins 1987; Cleyle et al. 1984). Wang et al. (2016a) have reported CO_2 atmosphere to be very beneficial for release of H_2S , COS and SO_2 into gas phase during pyrolysis, thus removing the sulfur from coals. Pyrolysis of refuse derived fuel (RDF) which is generated from municipal solid waste treatment plants is a temperature dependent energy recovery process (Manyà et al. 2015; Tippayawong et al. 2008).

Bicakova and Straka (2016) have co-pyrolysed waste tire/coal mixtures and reported the production of smokeless fuel/carbonaceous sorbent along with a high yield of tar and gases with high amount of hydrogen and methane. Melendi-Espina et al. (2015) have reported synergistic effect between coal and plastic wastes which changed the composition of the volatiles evolved, promoted interactions between the components and had negative effects on coal fluidity. Montiano et al. (2016) have carried out pyrolysis of two types of coals, sawdust and coal tar and reported independent thermal decomposition of the components without any apparent synergism and Alias et al. (2012) also found similar results during co-pyrolysis of the coal and Refuse Derive Fuel (RDF). Lei et al. (2016) have reported pretreatment of lignite coal with ionic liquids at low temperature leading to the increase in yield of oil fractions in the products. Tyler (1980) have reported flash pyrolysis of bituminous coal in a small scale fluidized bed reactor with an increase in the yield of CH_4 in H_2 atmosphere. Rizkiana et al. (2016) have reported an improvement in the quality of co-pyrolysis oil of low-rank coal and biomass in presence of Mg-modified ultra-stable Y type zeolite. Whyte et al. (2015) have reported the formation of catalytic bio-oil from pyrolysis of RDF char and oyster shell with similar density, heating value and viscosity as conventional diesel fuel. Tang et al. (2015) have reported an interactive effect during co-pyrolysis of Shenmu coal and cotton stalk leading to an increased tar yield. Vamvuka et al. (2003) pyrolysed olive kernel, forest and cotton residues mixed with lignite coal and reported higher thermochemical reactivity which make them 'solid biofuels'

which can produce faster and higher quantity of volatile compounds in fast kinetics.

2.3 Municipal solid wastes

Pyrolysis of municipal solid wastes is an attractive alternative to incineration for energy and resource recovery (Chen et al. 2014). The product yield and composition is affected largely by the feedstock, the pyrolysis temperature, the heating rate and the type of reactor adopted (Han et al. 2015; Nurul Islam et al. 2005). Several studies have been reported for the influence of synergetic interactions during co-pyrolysis of various feeds. Zuo et al. (2014) have conducted co-pyrolysis of sewage sludge and popular sawdust and reported characteristic change in the top phase oil due to the synergetic reactions that took place during co-pyrolysis. Zhou et al. (2014) have co-pyrolysed orange peel, tissue paper and PVC from MSW and reported that the production of alkyls and alkenes was inhibited during pyrolysis at low temperature and residue increased. Zhou et al. (2015b) have reported intense interactions between PVC and rice, poplar wood, tissue paper, wool, terylene, and rubber powder during their co-pyrolysis leading to promotion of low temperature pyrolysis. Fang et al. (2015) have co-pyrolysed paper sludge and municipal solid wastes in different proportions and different heating rates and reported an increase in the initial temperature with increase in paper sludge proportion. Ren et al. (2009) have conducted co-pyrolysis of cotton stalk and municipal solid wastes with high ash content and low calorific value and reported an increase in weight loss as well as NH_3 emissions with an increase in mass proportion of stalk. Wang et al. (2016b) have reported co-pyrolysis of microalgae and sewage sludge as a promising way to decrease feedstock cost and realize alternative fuel production and to avoid the high ash content and low heat value.

A few negative synergistic effects have also been reported in literature. Kim et al. (2010) have reported negligible interactions between the components of the feed during the co-pyrolysis of different components of municipal solid wastes (polyethylene, cellulose, lignin and sawdust from vinal wood). Wu et al. (1997) have reported insignificant effect of interactions on the rate of pyrolysis of paper mixture from

municipal solid wastes. Chen et al. (2016b) have reported negative synergistic effects during the co-pyrolysis of pork and polypropylene leading to hindered rate of pork pyrolysis and lower weight loss of the blends than the individual feeds. Fang et al. (2016) have studied the effect of MgO (magnesium oxide), Al_2O_3 (alumina) and ZnO (zinc oxide) additives and reported reduction of initial temperatures and activation energies. AlOthman et al. (2011) have reported the formation of activated carbon with high adsorption efficiency during co-pyrolysis of mixed solid wastes (biomass, cartons and polystyrene) at low carbonization temperatures. Cao et al. (2014) have developed a novel and improved waste pyrolysis test system with efficient rotary pyrolysis kiln working and high calorific power composite gas generation efficiency.

CONCLUSION

Pyrolysis can be universally applied to all sorts of carbonaceous wastes with excellent energy and material recovery. The products obtained can not only be used as fuels due to their high calorific value, but also can be a source of many valuable chemicals required in industry. Due to mass and volume reduction to great extent, it can lessen the pressure on land resources caused due to landfilling while the reaction time is very short and hence can be used in small systems with high throughput. Further research is required product upgrading and commercialization of the process. Co-pyrolysis can provide cheap and assuring approach for this purpose. More studies on the interactions of feeds during co-pyrolysis are required. The presence of halides, sulfides and heavy metals in the products can pose a severe challenge to the use of these products. Use of catalyst, microwave assisted heating, various pretreatment processes, efficient reactor design and optimum reaction conditions can improve the quality as well quantity of the desired products.

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