

ABSTRACT

Title of Dissertation proposal: INVESTIGATION INTO PYROLYSIS AND GASIFICATION OF SOLID WASTE COMPONENTS AND THEIR MIXTURES

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2021

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Unsustainable dependence on fossil fuel reserves for energy and material demands is leading to growing amounts of CO₂ concentration in the atmosphere and irreversible climate changes. Carbon neutral sources such as abundant biomass reserves and landfill-destined high energy density wastes such as plastics, and tire-wastes can be utilized together for energy and material production for a sustainable future. Pyrolysis and gasification can convert these variable feedstocks into valuable and uniform synthetic gas (syngas) with versatile downstream applicability to energy, liquid fuels, and other value-added chemicals production. But seasonal availability, high moisture and ash content, and relatively low energy density of biomass can result in significant

energy and economic losses during gasification. Furthermore, gasification of plastic wastes separately was found to result in feeding issues due to melt-phase, coking, and agglomerative behavior leading to operational issues. To resolve these issues, co-processing of biomass with these plastics and rubber wastes was found to be promising in addition to providing synergistic interaction leading to enhanced syngas yield and inhibitive behavior in some cases and thus motivating this work. This dissertation provides a deconvoluted understanding and quantification of the source and impact of these interactions for better process performance and alleviation of inhibitive interaction needed to develop reliable co-gasification of feedstock mixtures. To achieve this, plastic and tire wastes were investigated separately and mixed with different biomass species using a series of feedstock arrangements to understand synergistic influence on the syngas yield and kinetics in comparison to mono-conversion. Influence of operating conditions such as feedstock composition, temperature and gasifying agent was also examined for desirable conditions of energy recovery and high-quality syngas yield. Lab-scale semi-batch reactor studies equipped with online product gas analysis, along with thermogravimetric studies were utilized to obtain insight into the products yield, kinetics, and energy conversion. These results provided a better understanding of the influence of feedstocks and their interaction on the syngas and process behavior. They address the knowledge gap in versatile feedstock-flexible gasifier development for efficient and reliable syngas production from varying solid waste and biomass component mixtures with minimal changes to the operating conditions.

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by

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Chapter 1: Introduction

1.1 Carbon cycle disruption

The advent of modern medicine and improved nutritional knowledge has helped to increase the average human age and global population that has resulted in increased use of available global resources. Coinciding with the industrial revolution, the global population increased from 1 billion in the 1800s [1] to over 7 billion by 2017. The global population is estimated to increase by additional 1 billion by 2030. Two hundred years of industrial revolution has provided rapid improvements to the human lifestyle aided by fossil fuel supply from the buried hydrocarbon reservoir formed over a span of million years [2]. The rapid nature of this development has caused rapid depletion of natural hydrocarbon resources as well as the impact of our actions on the use of these resources that are now recognized to be unsustainable, both for energy use and the environment. One such effect is the rapid rise in the atmospheric CO₂ from 280 ppm in the pre-industrial era (~1800s) to above 400 ppm today due to a rapid increase in fossil fuel combustion for unsustainable energy demands of the industrial society, see Fig. 1 [3,4]. The consequences were not considered until much later when the impact of this rise was visible in the form of steady increase in global temperature [5]. The pursuit of economic growth for the betterment of living standards has led to increased energy consumption and waste production.

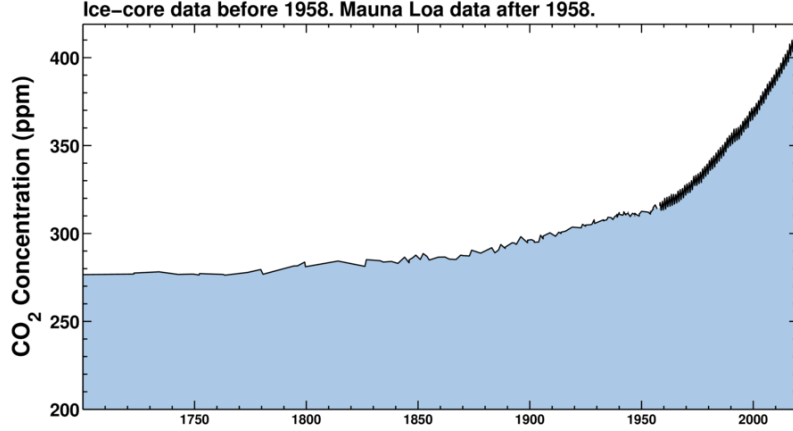
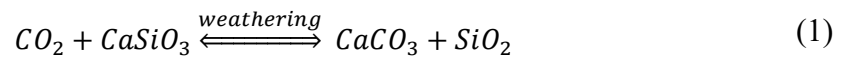


Figure 1. Rise in atmospheric CO₂ concentration with time [3]

1.1.1. Carbon cycle and its role

Understanding natural function of carbon cycle and its influence on the parameters responsible for providing habitable environment is necessary to recognize the impact of anthropogenic activities and its ability to cause imbalance in this cycle. Carbon cycle, similar to water cycle, refers to the flow of the elemental carbon in the form of different carbonaceous compounds such as CO₂, and CaCO₃ between the earth's atmosphere, land and water via chemical reactions.



The carbon cycle is stabilized by the weathering-metamorphism equilibrium along with carbonate deposition, given by Eq. (1) which controls the atmospheric CO₂ content [2,6]. Igneous rocks contain calcium oxide components in mineral phase which form metal carbonates when exposed to atmospheric CO₂ (weathering) [6,7]. These sediments are then eroded from the continents (land) to the oceans as the carbon sink. Geological carbon source for rise in atmospheric CO₂ is from natural degassing emissions from volcanic gases, and deep-sea hot spring fluids. An increase in global

temperature increases water vapor pressure causing accelerated hydrological cycles (freshwater runoff from continents into the oceans) [7]. This increased runoff leads to higher erosion rates so that fresh igneous rocks get constantly exposed to the atmosphere and increased weathering. Thus, the weathering carbon sinks becomes stronger when the temperature increases. An increase in atmospheric CO₂ also leads to increase in weathering rate and to increase the strength of the sink. This negative feedback, also called weathering CO₂ thermostat is partially responsible for stabilizing the atmospheric CO₂ content and the global temperature [8]. Any variations in the atmospheric CO₂ or global temperature causes the sink to become stronger to cause cooling of the planet and decrease the CO₂ content to a new set point. Over this time scale, the degassing emissions match the weathering to cause stabilized atmospheric CO₂. Note that the response time of this mechanism is in the order of hundred thousand years to reset the carbon balance [8].

An insight into the interaction between faster changes in atmospheric CO₂ on the global temperature can be understood by examining the interglacial cycles on change in the global temperature. The CO₂ levels have been constant over long time periods, averaged of the order of hundred thousand years, suggesting the influence of weathering CO₂ thermostat mechanism, although there have been interglacial cycles in CO₂ concentrations. The polar ice sheets also cycle through formation and melting driven by the change in solar intensity distribution caused by the earth's orbital wobbling, also called Milankovitch cycle [7]. Once ice sheets form, the diffuse reflectance of that surface changes to lower the energy absorption and thus the global temperature, which in turn increases the rate of ice sheets formation. This mechanism

has a positive feedback on the temperature change [7]. Decrease in global temperature causes increased ice sheets formation, which increases the reflected solar intensity to further lower the global temperature. The opposite effect occurs during ice melting. Another natural periodic mechanism that controls the atmospheric CO₂ is the atmosphere-ocean gas equilibrium. The temperature and pH dependence on the solubility of CO₂ in seawater is the pathway for control. Increase in ocean temperature leads to lower solubility and thus the dissolved CO₂ leaves the ocean into the atmosphere. This mechanism has the response time of the order of thousand years [7]. Lower temperature increases the solubility of CO₂ so that more CO₂ is captured by the ocean. Proxy global temperature and atmospheric CO₂ data showed that during glacial cycles the atmospheric CO₂ changed in rhythm with the temperature that accounted for a positive feedback mechanism in the carbon cycle causing a direct link between the CO₂ and global temperature [9]. Even though ocean-atmosphere CO₂ equilibrium is a positive feedback mechanism, it has been found that its contribution, based on deep sea data, does not fully account for the interglacial variation in CO₂ when temperature varied [7]. The variation in pH due to the variation in CO₃²⁻ ions also influences ocean's feedback on atmospheric CO₂. CO₂ reacts with water to form carbonate and bicarbonate ions so that increase in CO₂ intake decreases the pH of the ocean, also called ocean acidification. This acidification also increases the solubility of CaCO₃, which can then affect the marine life and the sustainability of CaCO₃ shells. The increase in acidity can also affect the marine life in other ways due to the changing conditions. All these natural inorganic processes along with significant biological contributions from marine and terrestrial life control the atmospheric concentration of CO₂ and the global

temperature. Change in any of these parameters affects the rest of the climate as per the above described cycle.

Table 1. Carbon pools of the earth (from [2])

Carbon Pools	Quantity (Gt)
Atmosphere	720
Oceans	38,400
Total inorganic	37,400
Total organic	1,000
Surface layer	670
Deep layer	36,730
Lithosphere	
Sedimentary carbonates	$> 0.6 \times 10^8$
Kerogens	0.15×10^8
Terrestrial Biosphere (total)	2,000
Living biomass	600-1,000
Dead biomass	1,200
Aquatic biosphere	1-2
Fossil fuels	4,130
Coal	3,510
Oil	230
Gas	140
Others (peat)	250

1.1.2. Rise in CO₂ emissions via fossil fuel dependence

Anthropogenic carbon emissions are mainly contributed from fossil fuel combustion to meet the energy demands. Fossil fuels are carbonaceous deposits in the crust of the earth that have formed over a span of millions of years. While the formation rate of these fuels has been long, their consumption rate, by humans, has been of the order of decades. Such a drastic imbalance in the utilization rate makes anthropogenic carbon emissions so rapid that the only natural carbon sequestration from atmosphere to land, i.e. photosynthesis, has been slow to catch up. Note that, even in the case of high wood

yield trees such as pine wood for example, 10 tons/yr/acre of wood is harvested which corresponds to net CO₂ absorption of only 3.63 tons of C/yr/acre via photosynthesis [10,11]. This is the main reason for net rise in atmospheric CO₂ content. The carbon emissions of ~9.8 Gt of C yr⁻¹ (in 2014) have been significant compared to the natural carbon fluxes [12,13]. The anthropogenic CO₂ flux should be compared only with the natural degassing flux since that is the only known natural and significant pathway for carbon movement from the crust into the atmosphere. Table 1 provides carbon pools of the earth. Isotopic studies have shown that the anthropogenic CO₂ is the main contributor for increases in the atmospheric CO₂ content. The rate of increase in atmospheric CO₂ was found to be only half that of the anthropogenic carbon emissions rate, which suggests that the rest of the carbon is missing. Carbon flux balancing showed that most possible pathway for missing CO₂ is into the ocean, which the ocean can adjust by increasing its pH [14,15]. Currently the global carbon cycle's negative feedback is keeping the atmospheric CO₂ to the present levels. Due to the order of ocean-atmosphere equilibrium time scale, it is expected that around the turn of this century, the ocean carbon pool may saturate causing other positive feedback mechanisms to drive significant climate changes. Predictions into the future is not very clear, but the presence of positive feedback mechanisms and their influence on the sensitive ecosystem makes this rising atmospheric CO₂ an essential problem of this century. It also provides a deciding factor for the future on the fate of life on the earth. Significant overhaul of the existing infrastructure and the methodology of problem solving is necessary prior to moving into such uncertain times. Even though the improvement of global lifestyle is necessary, it should not come at the expense of facing

the consequences of an unsustainable society, which deteriorated the climate of the planet into an uninhabitable place.

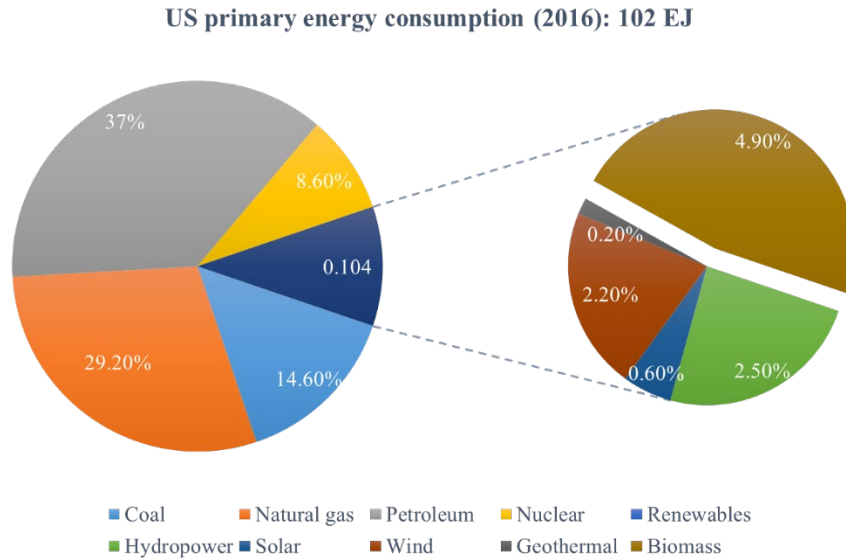


Figure 2. Primary energy consumption in the USA in 2016 [16]

The developed countries have driven industrialization from utilization of fossil fuel resources that have left large footprint on continuously increasing CO₂ as mentioned above due to lack of understanding on the consequences of carbon cycle disruption along with an underestimation of the population growth. Even in the developed countries such as the USA some 81% of primary energy consumption was from fossil fuel resources in 2016, see Fig. 2 [16]. This represents a significant amount (some 36 million barrels of oil equivalent/day) that needs to be replaced for sustainable and low-impact human existence. With climate change concerns clouding the fossil fuel usage due to their inherent inability to serve as sustainable source calls for alternate clean and sustainable fuel and energy production. While major growth in hydroelectric power plants took place to meet the need for renewable energy production, its availability on

global terms is rather limited. Its scalability to offset the fossil fuel usage without major replacements in the available infrastructure, especially in transportation and industrial sector, is limited. A radical surge in the development of clean, sustainable, and scalable renewable energy production is necessary to offset the fossil fuel contribution which currently aggregates to near 90% of the world energy consumption. Biofuels and waste correspond to only about 10% and hydro energy correspond to some 2.4% world energy consumption.

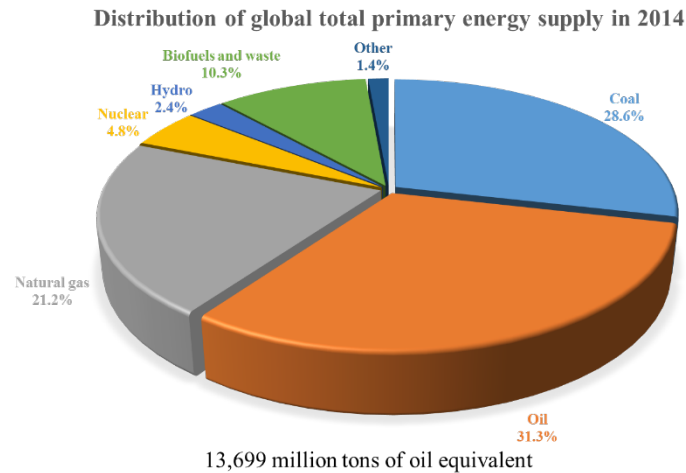


Figure 3. World primary energy supply in 2014 [17]

TOTAL MSW GENERATED IN THE USA IN 2015 (262 MILLION TONS)

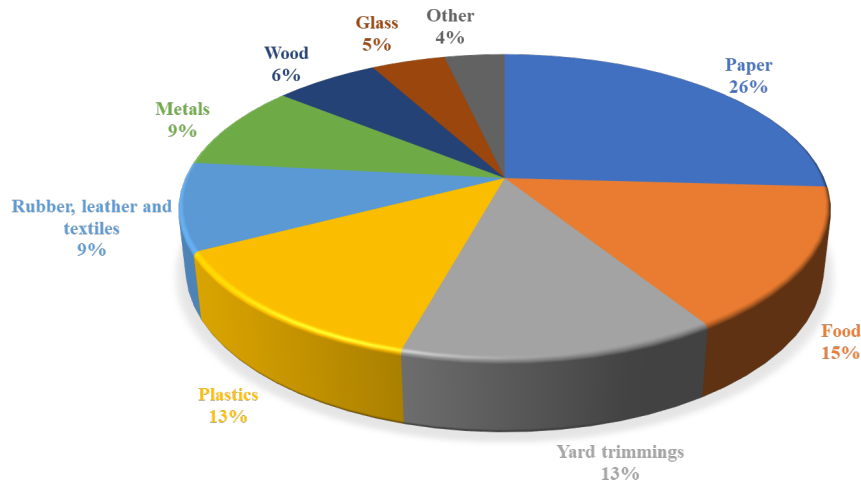


Figure 4. Typical composition of municipal solid wastes in the USA [18]

MSW MANAGEMENT IN THE USA IN 2015

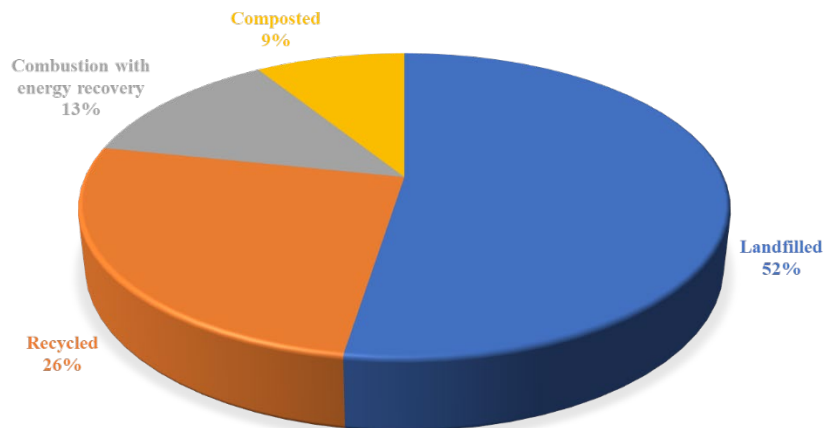


Figure 5. Fate of municipal solid wastes in the USA [18]

1.2 Growing Wastes and difficulties in recycling

Parallel to the issue of fossil fuel usage for energy and fuel production, the solid waste disposal issue is also on the rise with the continuous increase in world population. The

continuously increasing amounts of waste generation are not being balanced by the similar efforts on rate of recycling or recovery. Municipal solid waste is one of the leading forms of waste. Typical major components of MSW and their contribution are given in Fig. 4 [18]. While waste components such as those of metal and glass can be recycled, these components in 2015 corresponded to only 13% of total MSW in the USA. Most of the remaining materials are either reformed to energy via combustion or discarded to landfills. On an aggregate, more than 50% of the solid wastes are discarded into landfills in the USA, see Fig. 5 [18]. The composite nature of these wastes is causing difficulties both physically and economically for efficient recycling. The lack of appropriate and scalable recycling infrastructure for waste segregation, separation and recycling and the presence of planned obsolescence in products development is leading to these unprecedented and unacceptable statistics as in Fig. 5. Material management is necessary for a sustainable society and this is lacking in the present scenario. Significant portions of energy intensive materials, such as plastics and food waste, are ending up in landfills. Increase in rubber tire production from rapid growth of auto industry has also led to the evolution of more than 4 million tons of waste tires in 2017 in the USA. From this amount about 18.6% were land-disposed [19]. Globally, approximately 1 billion tires were disposed in 2017 [20,21]. World demand for tires is projected to increase by some 4.9% per year to 3.2 billion in 2022 [22]. Traditional ways for their disposal include re-use in construction, material recovery for carbon black, and energy recovery via combustion [23]. However, the disposal of tires in landfills is still a common practice due to its ease of disposal but it is an environmentally harmful and unsustainable pathway [24]. Landfilling is inexpensive

option in the short term but unattractive for waste management since significant land wastage along with potential chemical leaching from the landfills makes the soil around these landfills unusable. Furthermore, it often causes hazardous discharges to the water sheds that causes problems to clean water supply. Uncontrolled decomposition of organic wastes in landfills, especially manure waste causes methane release into the atmosphere leading to greenhouse effect, similar to CO_2 but methane is roughly 30 times more potent as a heat-trapping gas to provide enhanced greenhouse gas emission potential. To mitigate or avoid such influences on climate change, proper disposal practices of these wastes are necessary. Note that, significant portions of these wastes emanate from municipal solid wastes (MSW). As per EPA, the USA produced 262 million tons/annum of MSW in 2015 that consisted of materials shown in Fig. 4 [18]. This is equivalent to producing approximately 6 billion tons of MSW globally if global lifestyle was equated to that of the USA. While approximately 30% of this waste was recycled or composted (an accepted pathway for waste management), more than half of the total waste still ended into landfills, see Fig. 5 [18]. This represents a significant amount of chemical energy left unused, which could be extracted to meet energy demands. A detailed look into landfilling of several major components in MSW is shown in Fig. 6. Note that significant portions, representing more than 75% of plastics, and more than half of rubber, textiles, and leather wastes, end up in landfills. This is hazardous for the environment since organic wastes, such as food wastes, end up 3 out of 4 portions in landfills and their decomposition occurs in an uncontrolled environment. They contribute to significant portions of CH_4 and CO_2 emissions into the atmosphere during their anaerobic digestion, leading to climate risks described

above. Waste to energy pathway is very critical since significant amounts of these wastes cannot be separated out for recycling or composting.

TOTAL MSW GENERATED IN THE USA IN 2015 (262 MILLION TONS)

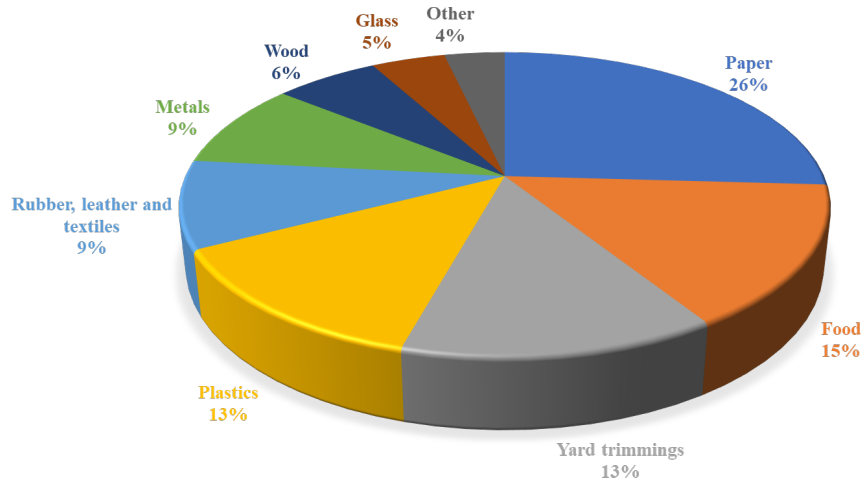


Figure 6. Distribution of MSW landfilled in the USA in 2015 [18]

1.3 Need for sustainability for restoration of carbon cycle

With the knowledge gained on understanding of the impact of carbon footprint, it is time to foster further investment in sustainable resources as replacement for fossil fuel consumption for energy and valuable chemicals production. Most of the global population resides in the so called ‘developing’ economies. It is very timely for all economies, including industrialized countries, to develop and cultivate sustainable pathways for energy and environment to foster improved lifestyles for all. Energy is the fundamental and most important resource needed for societal development. The fundamental requirement of a sustainable energy resource lies in its ability to recover energy at the same rate as its consumption. Renewable energy resources such as direct solar energy utilization, hydropower and geothermal energy, and wind energy are abundant and driven by the solar radiation and earth’s energy. Their abundance negates

the need for recovery. France, Slovakia, Ukraine, Belgium, and Hungary use nuclear energy for majority of the country's electricity supply [17]. Other resources, such as biomass energy, needs recovery time which is the time taken to grow the same number of resources as consumed over a given time span. Even though photosynthesis is relatively slow, it extracts solar energy to form well known form of carbon-based lignocellulosic material at higher efficiency than photovoltaics and the growth of biomass is necessary for the survival of ecosystems. This makes simultaneous plantation and utilization of biomass a sustainable pathway for energy production. The fuels produced from biomass are also carbon based similar to fossil fuels, which means the infrastructure replacement and the understanding needed for their implementation is lower compared to other renewable forms of energy production. Following, we can discuss biomass and its potential to meet our goal of greater energy demands globally.



Figure 7. Classification of feedstock based on the source

Lignocellulosic material	Cellulose (dry wt. %)	Hemicellulose (dry wt. %)	Lignin (dry wt. %)
Hardwood stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper	85-99	0	0-15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspaper	40-55	25-40	18-30
Waste papers from chemical pulps	60-70	10-20	5-10
Primary wastewater solids	8-15	NA	24-29
Swine waste	6	28	NA
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12

Figure 8. Typical lignocellulosic content in the various feedstocks [25]

1.4 Biomass as a sustainable energy resource

The biomass and carbonaceous solid or sludge wastes given above can be broadly classified based on the source of feedstock generation, see Fig. 7. While this classification helps in realizing the sources, a more detailed classification is necessary that includes more detailed parameters of the wastes, such as composition and energy content. Woody biomass, paper and agricultural residue and other biomass and bio-wastes can be characterized as lignocellulosic biomass due to their composition constituting predominantly as cellulose, hemicellulose, and lignin. Typical biomass and waste types and their lignocellulosic content is given in Fig. 8 [25]. Although these biomasses are similar in their generic lignocellulosic content, they may vary significantly in the pre-processed moisture and ash content, and thus energy content which significantly dictates the processing technique suitable for their reformation to energy, fuel or value-added chemical products.

Contribution of variety of biomasses to bioenergy in 2008

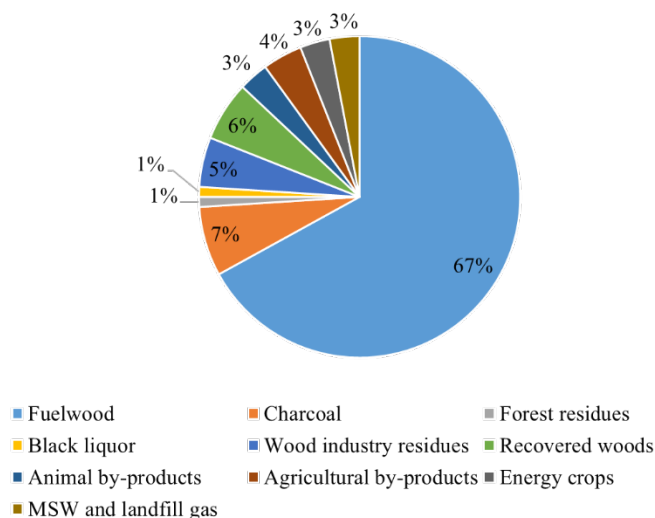


Figure 9. Contributions of different types of biomasses to global bioenergy [26]

Currently, world's biomass based energy, also called bioenergy, contributed to 50.3 EJ/yr in 2008 which is ~10% of the global primary energy consumption [26]. Figure 9 shows the contribution of a variety of biomass sources to total primary energy production in 2008 [26]. This bioenergy usage estimates include two generic types of usage. First, bioenergy in the form of direct burning of wood, dung, and straws for cooking, space heating and lighting in the rural areas of 'developing' countries. This accounts for around 37-43 EJ/yr of usage while its low conversion efficiency means that only about 10-20% of this energy reaches the consumer. This shows the availability of resources but lack of available infrastructure for sustainable utilization. Second, bioenergy in the form of electricity and CHP, space heating, and transport fuels (ethanol and biodiesel) from biofuels such as wood, MSW and biogas) in a developed infrastructure at high efficiency accounts for about 11 EJ/yr of primary energy consumption. Note that only up to 60% of this energy reaches the consumer after considering losses from process efficiency in conversion to secondary energy [26].

Table 2 shows the details of these estimates that shows the stark differences in the improvements that can be obtained with appropriate infrastructure. Modern bioenergy infrastructure reduced the primary energy requirement by three times for the same amount of secondary energy production. Countries such as India, China and Brazil were shown to be the major contributors to bioenergy production [27].

Table 2. Global bioenergy contributions from different sectors [26]

Type	Approx. primary energy (EJ/yr)	Approx. average efficiency (%)	Approx. secondary energy (EJ/yr)
Traditional biomass			
Accounted for in IEA statistics	30.7	10-20	3.6
Estimated for informal sectors (ex. Charcoal)	6-12		0.6-2.4
Total	37-43		3.6-8.4
Modern bioenergy			
Electricity and CHP from biomass, MSW, and biogas	4	32	1.3
Heat in residential, public/commercial buildings from solid biomass and biogas	4.2	80	3.4
Road transport fuels (ethanol and biodiesel)	3.1	60	1.9
Total	11.3	58	6.6

The theoretical potential estimates on global bioenergy considering high biomass plantation productivity from global agriculture on land, and considering the need for conservation of a feasible biosphere, one global modeling study showed maximum bioenergy potential of 1,548 EJ/yr [28]. This is the amount of available biomass for energy considering only biophysical constraints. Assessing the technical potential is difficult to predict that accounts for biomass production with practice limitations, competition with food, fodder, fiber and forest products, area for human infrastructure, along with nature, and biodiversity preservations. This is primarily due to uncertainty in cropping techniques to be implemented, weather conditions, and difficulty in predicting the competition between the demands for forestry and agriculture products

(as mentioned above) with the demand for energy. Variations in the assumptions on population, economic and technological growth, variety in social preferences, climate change, and uncertainty of biodiversity causes the broadband in the estimates of technical potential by different studies. Table 3 provides the technical potential estimates by 2050 for each variety of biomass considered for bioenergy. Considering rain fed lignocellulosic plants on unprotected woodlands and grasslands while accounting for food and fodder requirements (excluding forests for biodiversity purposes) the global technical potential is estimated to be 171 EJ/yr [26]. Different plantation and crop management techniques may be considered to enhance the potential without disturbing biodiversity.

Table 3. Technical potential estimates of bioenergy from different sources by 2050

[26]

Biomass category	Comment	2050 Technical potential (EJ/yr)
Agricultural residues	By-products of agriculture: primary (cereal straw from harvesting) and secondary (rice husk from mills)	15 to 70
Dedicated biomass production on surplus agricultural land	Land used: agricultural land not used for food; Conventional agriculture crops and dedicated bioenergy plants Possibility of no surplus land availability from food sector development	0 to 700
Dedicated biomass production on marginal lands	Usage of deforested, degraded or marginal lands not suited for agriculture to grow biomass by bioenergy schemes, such as reforestation. Lacks appropriate definition of marginal lands and this means addition of surplus agriculture land and marginal lands may be double counting;	0 to 110
Forest biomass	Forest sector by-products- Primary: silvicultural thinning and logging Secondary: Wood processing residues- sawdust, bark Zero potential possible if the demand from other sectors such as paper, wood exceeds the estimates	0 to 110
Dung	Animal manure	5 to 50
Organic wastes	Household and restaurant organic wastes; discarded wood including paper, construction and demolition; Waste management critical	5 to >50
Total		<50 to > 1000

The technical potential estimates provide the importance of different kinds of biomass to meet our energy demands, even though these estimates do not always consider policy

and environmental limitations. This means efficient management and utilization of bioenergy is important to negate the continuously rising CO₂ emission. The issue with biomass for energy production lies in its low mass and low energy density as compared to fossil fuels. Their management in terms of harvesting, pretreatment, storage, and transport is estimated to have significant energy costs that can account for some 20-50% of total energy produced from them. The dependence of single type of biomass makes it unreliable due to their limited seasonal availability. This makes the contribution of various secondary bio-residues, such as rice husk, animal manure, and other biogenic wastes from MSW, important to achieve the highest potential to meet the energy demands in a carbon constrained world. Although these secondary residues can potentially provide energy, their conversion efficiency significantly depends on their energy content, which then also depends on their moisture content, chemical composition, and inorganic content. These factors decide the energy consumption for pretreatment of these feedstocks to enhance their compatibility to secondary energy carrier conversion techniques, such as combustion, gasification, pyrolysis, anaerobic digestion, or fermentation.

1.5 Wastes as supplement to biomass

Low energy density of secondary biomasses along with varying amounts and types of wood production demand causes unreliable availability of biomass feedstocks. Even the supplementary energy feedstocks required for the bioenergy potential mentioned above are not as reliable for biomass feedstocks. It is recognized that there is potential for biomass replacing fossil fuels in the energy sector, but their potential in replacing the petrochemical precursors used in today's world to produce value-added chemicals

and polymers is uncertain and mostly unknown. With reasonable technical assumptions, the bioenergy is only able to supplement coal and natural gas for energy production, but fossil fuels would still be required for transportation and plastics production. This implies that while consideration to only bioenergy consumption along with other conventional renewable energies for carbon emissions, biomass do not account for the potential carbon emissions from fossil fuel usage in materials requirement.

Plastics materials are produced from fossil fuels and their consumption is steadily increasing. Carbon material balance is very important for sustainable utilization of resources. An important solution here is to develop synergy between bioenergy utilization and plastic waste management as a hybrid approach in managing both biomass and plastic wastes. Low moisture content in these plastic wastes helps to justify ignoring its moisture content as an important parameter unlike in biomass wastes wherein widely different amounts of moisture can be found, up to 80% by weight. Waste components such as plastics, rubber, and textiles are high energy density materials, and their utilization offers necessary supplements to biomass for fossil fuel replacement in both energy and materials production. Note that biomass alone does not show potential for complete fossil fuel replacement when considering both energy and material production. Tire wastes have a heating value higher than coal and contains considerable amount of carbon black. Therefore, energy, fuels and materials recovery from these high-quality wastes can help increase their value and while providing sustainable energy supply and a sustainable solution to waste tire disposal [29].

Thermochemical conversion can be utilized in this regard for conversion to syngas, oils, and other value-added chemicals and high-value carbon products.

1.6 Thermochemical Pathways

The thermochemical processes, well known to mankind for centuries, involves conversion of biomass feedstocks into valuable products such as fuel, heat or electricity at high temperature. Direct combustion is one of the dominantly used process for biomass utilization in the current scenario, especially in rural areas involving burning of charcoal, wood, or dung cakes for cooking and heat. Thermochemical conversion is the most versatile pathway for biomass and waste utilization because chemical and biochemical conversion techniques, as mentioned above, are not capable of converting wide range of feedstocks. Since the driving potential in these processes is temperature, unlike difference in chemical potential or microorganism metabolism in chemical and biochemical processes, these reactions provide high throughput along with feed flexibility, which is necessary to utilize wastes for bio-energy production from biomass. Biomass combustion is a well-established technique involving burning of biomass or wastes in the presence of air/oxygen for heat production which can be utilized for combined heat and power. While this technique is well-known, solid combustion, especially biomass and wastes with low heating value, it is inefficient due to lack of mixing and low specific heat output causing low temperature operation, incomplete combustion and excessive pollutants formation and emission. Direct combustion of these heterogeneous oxygenated feedstocks also produces NO_x, SO_x, and other pollutants due to the high reactivity of oxygen, and presence of nitrogen and sulfur in feedstocks [30,31]. Removal of these pollutants is not only difficult, but also energy

intensive that only lowers the net efficiency of direct combustion. Pyrolysis and gasification processes provide better control along with uniformity in the products produced. Lower oxygen content during pyrolysis and gasification results in off gases produced to contain lower nitrogen oxide and sulfur oxide compounds. The N and S content leave as NH_3 and H_2S that are easier to separate out using processes such as wet scrubbing [32]. In this chapter, we focus on pyrolysis and gasification as the primary components of thermochemical processing.

Table 4. Thermochemical processes and their product yield by temperature and residence times [33]

Process		Temperature	Vapor residence time	Liquid yield (% wt.)	Solid yield (% wt.)	Gas yield (% wt.)
Pyrolysis	Fast pyrolysis	~773 K	~1 s	75	12	13
	Intermediate pyrolysis	~773 K	10-30 s	50% in 2 phases	25	25
	Carbonization	~673 K	~hours to days	30	35	35
	Torrefaction	~563 K	Solid residence time ~ 10-60 min	5% if condensed	80% solid	20
Gasification		>973 K	Same as char	5	10	85

Thermochemical processing of carbonaceous materials can be classified based on the operating parameters such as temperature, heating rate, vapor residence time, gasifying agent during pyrolysis and gasification. Their product yield depends critically on the above parameters. Role of these parameters in pyrolysis and gasification can be seen from Table 4. Solid product produced from these processes is called char, which is a coal like product with high heating value, high C content, and includes the inorganic residue left after decomposition. Gaseous products formed primarily include CO , CO_2 , H_2 along with low molecular weight (C_1 , C_2 and C_3) hydrocarbon gases. Their relative

yield depends on the above mentioned operational parameters along with material composition [31]. Liquid yields are called bio-oil/pyrolysis oil in the case of pyrolysis and tar in the case of gasification. They contain wide variety of products including oxygenates, carboxylic acids, aldehydes in the case of bio-oil (from pyrolysis) and PAHs in the case of tar (from gasification) [33].

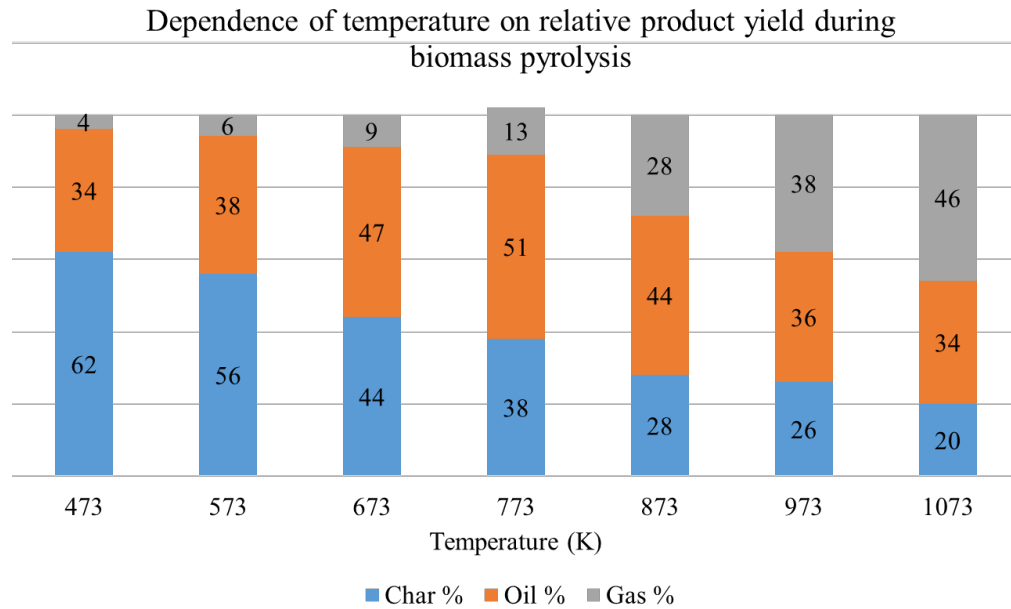


Figure 10. Effect of temperature on fast pyrolysis and relative product phase yields [34]

1.6.1 Pyrolysis

Pyrolysis is the process of decomposing any material by heating to high temperatures to break its chemical bonds in the absence of oxidizing agents such as air/O₂, steam, or CO₂. This contrasts with gasification that includes some oxidizing agent. Pyrolyzers can be operated under different conditions for improved yield and increased selectivity of the desired product phase and amounts. Typical kinds of pyrolysis pathways explored for different amounts of gas/liquid yields are presented in Table 4. Solid

biomass upon heating releases vapors from material decomposition. The vapor residence time is the time these vapors evolved from the biomass decomposition stay in contact with the solid phase during pyrolysis. This controls the secondary reactions of evolved vapors with the solid components, which further controls the extent of cracking. Temperature controls the thermodynamic extent of reaction. Farther downstream higher gas yield results from enhanced cracking. Low temperature and long residence times favor solids formation in the form of char. High temperature and long residence times favor formation of gases as this results in high degree of cracking. However, moderate temperatures and shorter residence time yield liquid formation, usually called bio-oil. The short residence times also consider the contact time on char formed which needs to be reduced to avoid cracking of vapors into low molecular weight hydrocarbon gases. The influence of temperature on biomass pyrolysis is shown in Fig. 10 [34]. Optimal temperature for high bio-oil yield is seen to be around 773 K, which balances the repolymerization and the extent of cracking. The low temperature operation and long residence times leads to enhanced repolymerization to form increased char yields from carbonization. Biomass carbonization or a lower temperature torrefaction, is conducted to obtain processed solid fuel with higher heating value and density from a biomass having low density and low heating value. The obtained torrefied biomass can be pelletized into high density solid fuel for easy transportation and enhanced combustion efficiency when combusted for heat/power. These solid fuels contain high carbon content and can act as substitute for coal in various applications, especially for power generation.

Fast pyrolysis occurs at vapor residence times as low as 2s at moderately low temperatures of 773 K with the motive to yield high bio-oils. To avoid secondary vapor phase reactions and reach thermodynamic non-equilibrium, the collected vapors undergo rapid cooling to obtain high yields of bio-oil. Vapor quenching efficiency can be enhanced by collecting vapors in an immiscible hydrocarbon solvent. The high heating rate requirement limits the feedstock properties to moisture content less than 10% and small particle sizes (around 2mm or less) as heating of this biomass is the rate limiting step in fast pyrolysis. It also helps to reduce aqueous content in the bio-oil. When lignocellulosic biomass is pyrolyzed, the lignin derived species are inherently more stable due to high aromaticity (lignin being aromatic polymer) and this means low gas yields from lignin. Lignin pyrolysis leads to phenolic derivatives such as guaiacol. Cellulose pyrolysis leads to dehydration and depolymerization leading to levoglucosan if the heating rates are low. At high heating rates, anhydrosugars, such as levoglucosan, can be minimized favoring production of liquid products.

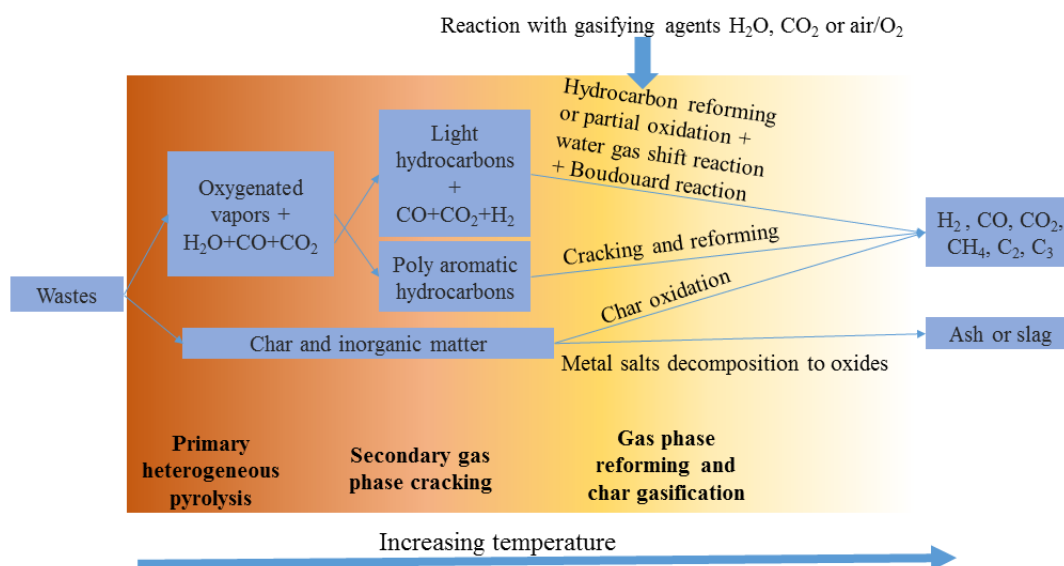


Figure 11. Simplified reaction pathways in gasification

1.6.2 Gasification

Gasification is pyrolysis of solid carbonaceous feedstock in the presence of gasifying/oxidizing agents such as steam, CO_2 or O_2/air at high temperature (> 1000 K). This process is developed to obtain high yield of synthesis gas, which is a mixture of H_2 , CO , CO_2 , H_2O , CH_4 and low molecular weight hydrocarbons (C_2 , C_3), and minimum yield of tar or char (liquid and solid yields). Typical reaction pathway involves pyrolysis followed by secondary reactions among the vapors formed, reforming of the vapors using gasifying agent, in parallel with the gasification of char formed with the aid of gasifying agent to yield H_2 and CO , see Fig. 11. Side reactions also occur which involves repolymerization of the vapors to yield polyaromatic hydrocarbons (PAH). The solid feedstock initially is converted into oxygenated vapors including CO_2 , H_2O and CO along with char whose relative yield depends on heating rate and operational temperature. These reactions basically correspond to thermal decomposition via depolymerization and cracking reactions. This primary heterogeneous pyrolysis is followed by thermal cracking to reform to lower molecular weight hydrocarbons along with CO , CO_2 , and H_2 as well as side repolymerization reactions to form heavy molecular weight wax, such as polyaromatic hydrocarbons, also called tar, depending on the reactor operational temperature. Low temperatures favor the tar formation while high temperatures greater than 1300 K have reported no residual tar yields. This combination of low molecular weight hydrocarbons, along with the tar and char react with the gasifying agents to result in gaseous composition dictated by thermodynamic equilibrium. The major and simplified set of reactions governing final composition of gases formed is summarized in Fig. 12. For simplicity, the reaction

pathway is drawn linear. But the intermediates such as the oxygenate vapors can also react with either the gasifying agents, char or light hydrocarbons in complicated pathways of intermediate reactions.

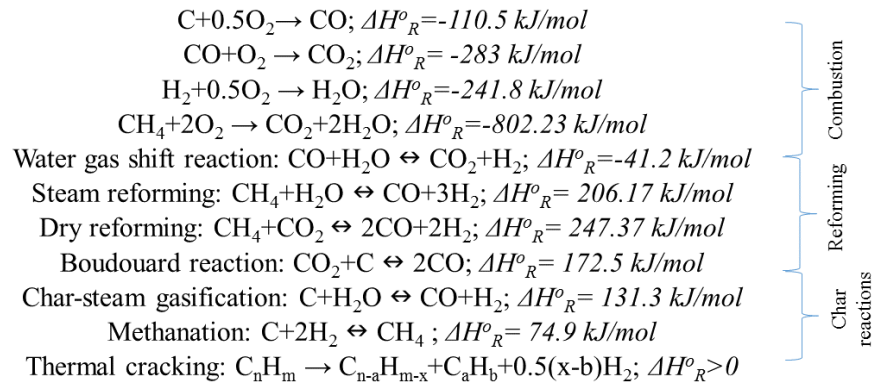


Figure 12. Major equilibrium reactions considered in gasification

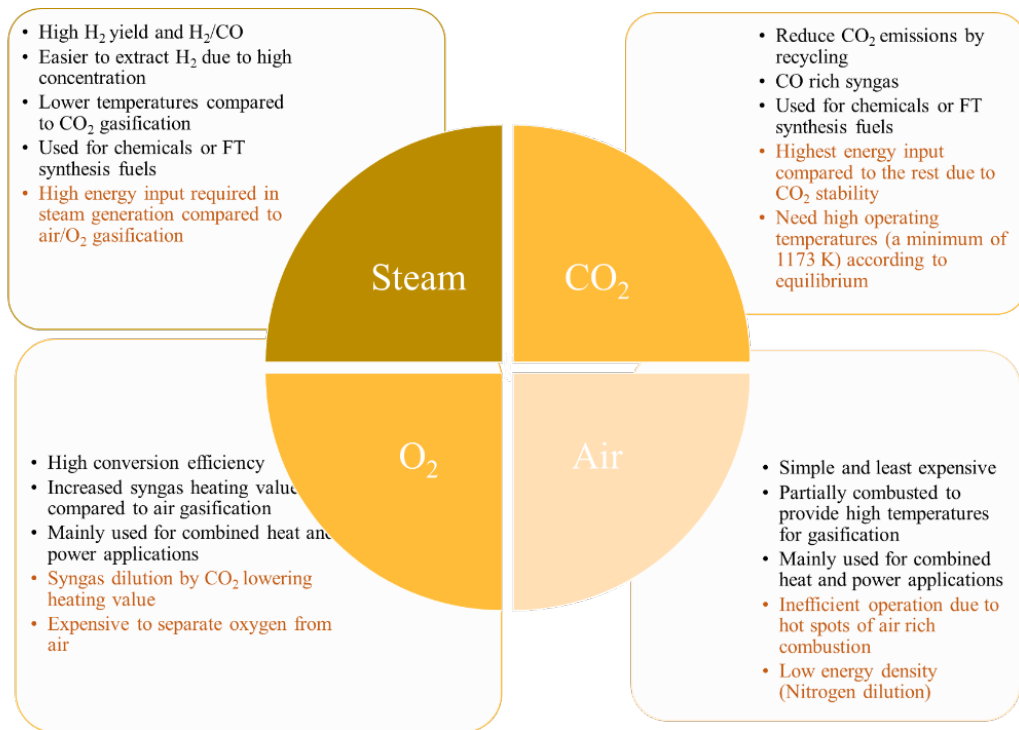


Figure 13. Effect of gasifying agent on the product yield with advantages and issues

[35]

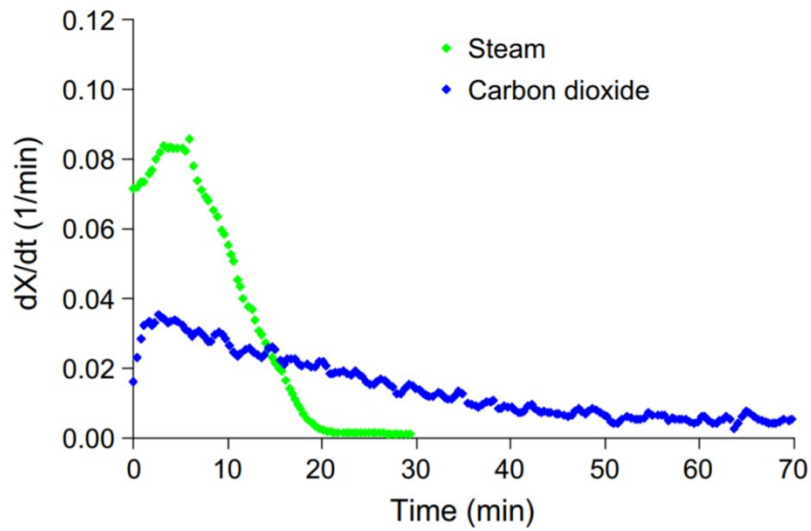


Figure 14. Evolution of conversion rate in gasification of food wastes using steam and CO_2 as gasifying agent (X = conversion and $T= 1173 \text{ K}$) [36]

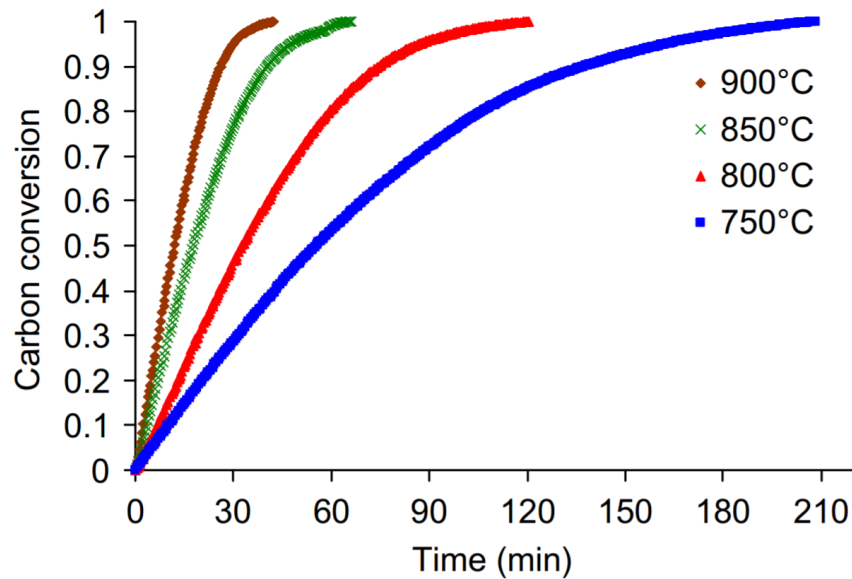


Figure 15. Carbon conversion rate of steam gasification of food waste for different temperatures [37]

The dependence of gasifying agent on the product yield and selectivity along with the advantages and disadvantages are summarized in Fig. 13. Comparison of gasification

rate of food waste using steam and carbon dioxide measured in a semi-batch reactor is shown in Fig. 14. In general, the gasifying agent is chosen depending on the downstream application or on the availability of reactants. Steam gasification can be used to gain syngas with high H_2 content while dry/ CO_2 gasification enhances CO content in the syngas. Steam or CO_2 gasification reactions are endothermic which can be maintained either by external heat or by using air/ O_2 at very fuel-rich conditions. The dependence of gasifying agent and temperature on the syngas composition can be found in ref. [38,39]. Effect of temperature on gasifying rates of food waste examined in semi-batch reactor is shown in Fig. 15. While operational temperatures can vary from 1000-1500 K for different gasifying reactors used, the industrial gasifiers often operate at low to atmospheric pressures. The reason for choosing low to atmospheric pressures is that, although high pressures enhance char gasification and lowers tar yields, it produces methane rich syngas which is less desired compared to H_2 and CO. High pressures also pose significant restrictions due to the material handling and high pressure feeding of the feedstock making it less attractive for industrial operational conditions. The experimental investigation of temperature dependency on gases yields have matched well with the equilibrium results due to the high temperatures at which gasifiers are operated resulting in equilibrium driven reactions.

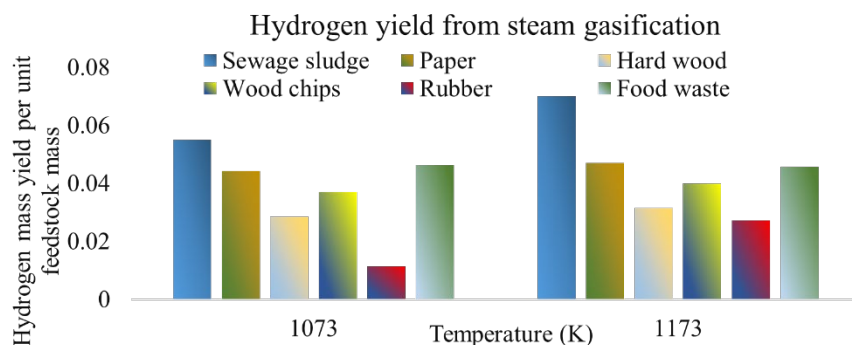


Figure 16. Hydrogen gas yield from steam gasification of different feedstocks for different temperatures [37,40,41]

The choice of feedstock also poses some limitations. Investigations into different types of feedstocks for gasification can be found in literature which include wood chips, pellets, paper and cardboard feeds, waste water sludge, chicken manure and others [40–43]. Figure 16 summarizes hydrogen gas yield per unit feedstock mass from steam gasification of different types of feedstocks in lab scale semi-batch reactor. The cumulative yield differed in both yield and the dependence of temperature depending on the type of feedstock used. Moderately high energy density is required from the feedstock before it reaches the gasifier. High moisture content feedstock such as municipal waste sludge, yard trimming, or food waste, makes the process extremely endothermic to significantly lower the energy efficiency of the process. Relatively low moisture content of 10% or less by mass is preferred to limit the energy consumption for drying within the gasifier to lower values as compared to the gasification reactions. High moisture content feedstocks are pre-dried either by sun drying, waste heat drying or electric drying. If the supplied feedstock straight from the source has very high moisture content, energy analysis is essential to determine if the energy consumption

for drying of such drying can be maintained by the gasification plant. Low grade feedstocks as above can be complemented by co-gasifying with high energy density wastes such as plastics, and rubber. Not only does this reduce dependence on the supply of feedstocks, but investigations into such gasification also reported synergistic effects increasing the syngas and hydrogen yield by mutual interaction. This can be seen especially between biomass such as wood chips and plastics such as polyethylene in ref. [44], but significant understanding about the interaction pathway for synergy is lacking in the literature. In the case of moisture diluted feedstocks, although such feedstock can be gasified, there are other thermochemical pathways such as hydrothermal processing which is inherently more useful and energy efficient to reform high moisture biomass. Other diluent that lowers the energy density of feedstock is inorganics that can be determined from its ash content. Ash content as high as 20% (based on dry mass basis) can be seen in feedstocks such as chicken or other animal manure, food waste and others [39]. This dilution does not have as significant effect on the energy efficiency as moisture dilution, but very high ash content complicates the gasifier design.

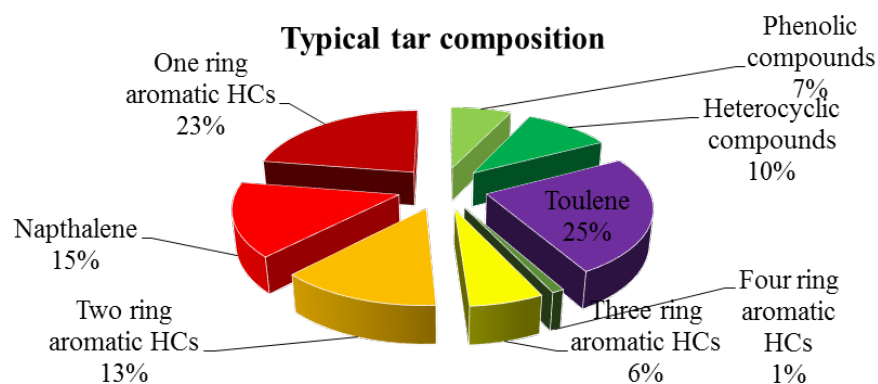


Figure 17. Typical composition of tar yield during gasification at relatively lower temperature [45]

One of the main issues of low temperature operation in gasification is the formation of tar, which effectively results in low carbon conversion to gaseous product yields. Tar content along with gaseous hydrocarbon content in syngas are not desirable products. Characteristic composition of tar is shown in Fig. 17 [45]. Tars must be avoided to limit clogging of pipes and loss of potential fuel energy yield along with avoidance of carcinogenetic emissions from the combustion of tar particles and improve the quality of syngas for fuel production, efficient combustion and for use in chemical plants. Different techniques for tar elimination have been explored [45–52]. Some of them include catalytic cracking or cracking on char bed, or thermal cracking by high temperature operation. These techniques were examined both in-situ over the catalytic fluidized bed in a gasifier or as part of downstream syngas cleaning. Downstream catalysts used for tar cracking are hydrocarbon active metals which are usually transition metals; most common being Ni, Pt, Pd, Ru, Rh, Fe supported on acidic and highly porous metal oxides such as alumino-silicates or zeolites, or zirconia and others. Alkali carbonates such as K_2CO_3 , Na_2CO_3 , and $CaCO_3$ were also reported to be effective in tar cracking. Petroleum research has also helped in this aspect. Examples include fluid catalytic cracking (FCC) catalysts such as ion exchanged zeolites (H-ZSM-5 and others) that have been found to be very effective with high activity towards tar cracking. In-situ tar cracking in the gasifier can be performed efficiently on mineral based catalysts such as dolomite, magnesite, calcite, olivine, clay minerals as they

although are lower in activity compared to synthetic catalysts, their availability, structural strength, and commercial feasibility makes them a much preferred option.

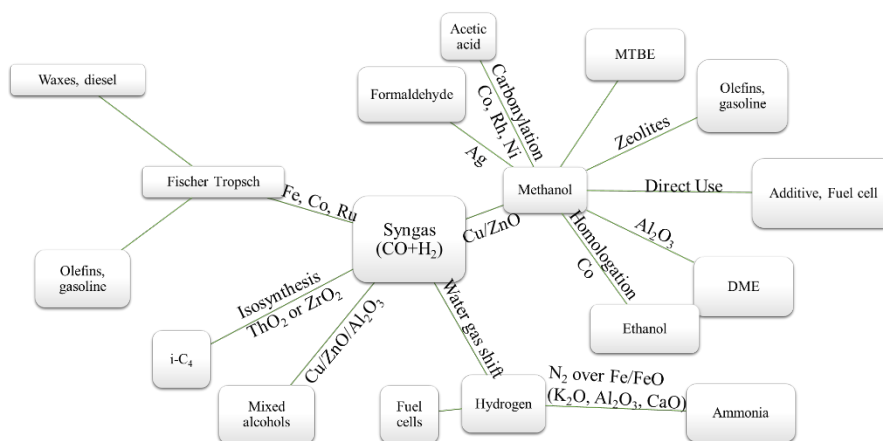


Figure 18. Syngas and its downstream derivative products [53]

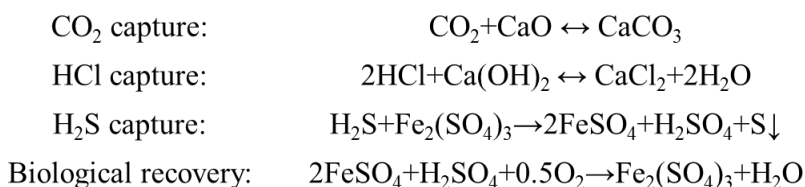


Figure 19. Chemical transformation during syngas cleaning [47]

Syngas is the product value of interest from gasification process. Syngas is a gaseous fuel with medium to high heating value that can be used for thermal energy production from the combustion of syngas. Syngas is an intermediate product that can be converted downstream to multiple high demand value added chemicals or liquid fuels that can be used for transportation fuels, see Fig. 18 [53]. Although heat or power generation does not need any complicated downstream processing other than particulate and char filtration, situation is much different for fuels or chemical synthesis. This varied use of syngas is dependent critically on its chemical composition especially H₂/CO molar ratio. Downstream cleaning and reforming of syngas includes catalytic cracking or

steam reforming of the gaseous hydrocarbons (CH_4 , C_2 and C_3) with the result being a combination of H_2 , CO and CO_2 . Water gas shift reaction follows to adjust the ratio of H_2/CO and H_2/CO_2 . For hydrogen production, complete water gas shift reaction is carried out leaving a mixture of H_2 with CO_2 . CO_2 in this mixture can be removed by physisorption basis using pressure swing adsorption or chemisorption basis using for example CaO for carbon capture as CaCO_3 as shown in Fig. 19 [47]. H_2 can also be separated from CO_2 using novel membrane separation techniques such as Pd based, holey graphene based and other novel membranes. This is an area of active research in the field of hydrogen production and H based fuel cells. Other impurities such as HCN , NH_3 , H_2S or HCl are also part of the raw syngas produced from extractive content such as amino acids and other impurities as observed by the Cl, N or S content from ultimate analysis of different biomass or waste samples [47]. These impurities can be removed either by dry scrubbing with conversion of $\text{Ca}(\text{OH})_2$ to CaCl_2 or amine solvent extraction. Wet scrubbing can also remove these impurities; for example, HCl is highly soluble in water and can addition of Na_2CO_3 enhances capture of HCl during wet scrubbing. Research is in progress on how to minimize the energy requirement and design complications while lowering waste streams as in wet scrubbing for syngas cleaning to remove these impurities with lower energy and reactant consumption/solvent recovery. Novel biochemical techniques are also under development such as, removal of H_2S by reacting with $\text{Fe}_2(\text{SO}_4)_3$ which can be regenerated by biological oxidation with the help of *Thiobacillus ferro-oxidans* [47]. Final products from syngas can be chosen depending on the market requirements, see Fig. 18. Fisher-Tropsch synthesis is useful as the product offers a replacement for all

kinds of transportation fuel with almost no additional energy required for the synthesis of the syngas [54]. The emissions from burning such fuels are essentially from sequestered by the flora which completes the carbon cycle in a shorter time scale making the process sustainable. Hydrogen production from syngas for fuel cells can also provide a clean energy option for mobility but considering the existing infrastructure and its ability to accommodate FT fuels make it an ideal pathway provided one can suffice with the other energy parameters required and feedstock availability.

1.7 Need for co-processing

In both fast pyrolysis and gasification, use of biomass as feedstock poses some limitations. Low moisture and high energy contents are required for both these processes. High oxygen content in the feedstock lowers the stability of bio-oil and poses restrictions in its usage due to acidity, high melting point, and high viscosity which leave bio-oil with significant downstream processing requirements before its utilization as fuel [33]. In gasification, high carboxylic acid content in biomass leads to high CO₂ evolution, which dilutes the syngas produced and lowers its energy density. Also, seasonal availability of biomass poses restrictions on the reliability of biomass for gasification [26]. Similarly, conversion of MSW wastes that includes plastic wastes also has some limitations for waste processing by gasification [55]. Significant research on pyrolysis and gasification of plastics has been reported, especially mixed plastic wastes [55–63]. The issues relating to gasification and pyrolysis of plastics alone arise from product composition and the reactor design requirements. Pyrolysis of plastic wastes alone increases the corrosive and toxic properties in bio-oil by yielding products

such as HCl, benzoic acid, and significant tar which lowers the quality of bio-oil [64]. Plastic feeding also poses technical difficulties in reactor design due to their flowing nature and flammability along with agglomerative behavior on bed materials in fluidized bed reactors [64].

A novel proposed alternative for utilization of biomass and recovery of plastic wastes is to develop synergy between their purposes and this can be made possible by co-processing blends of biomass and plastic wastes. Significant advantages can be gained from such co-processing in both pyrolysis and gasification [64]. These include:

1. The high heating value of plastic wastes can supplement the secondary biomass (such as rice husk, manure waste) with mediocre heating value, to support gasification without the need for energy intensive moisture removal from biomass and provide consistent syngas yield.
2. Unreliable biomass availability due to their seasonal production and availability can be minimized as the plastic wastes can be used as supplements to blend in and stabilize with the feedstock supply and thus allow for stable syngas yield throughout the year in all seasons.
3. Addition of biomass to plastic wastes increases the control over feedstock feeding into the reactor by binding it together and allowing for efficient reactor design along with minimizing agglomerative behavior from the sticky and viscous behavior of plastic wastes when heated which causes feeding issues and defluidization, see Fig. 20 [65].

4. Co-processing also decreases the need for waste separation, especially in the case of separating plastic wastes from food, paper and wood wastes that only decreases the waste management efficiency and increases costs.
5. The relatively low O/C and high H/C in plastic wastes compared to bio-feedstocks decreases the net oxygen in biomass-plastic blends so that fast pyrolysis of these blends yielded bio-oil with better quality in terms of stability, viscosity, and acidity due to low oxygen content in the oxygenates in the bio-oil. They all help minimize the requirement of downstream processing of bio-oil before their further usage.
6. Coking that occurs during feeding of plastic wastes (polyethylene terephthalate) into air-blown fluidized bed gasifier was found to be reduced by blending the plastic waste with wood and biomass-plastic composite pellets that provided enhanced heat transfer and fluidization.
7. The possibility of synergistic effects between biomass and plastic components (to be discussed in the next chapter) which were found to provide increased cracking and thus synergistically higher H₂ and total syngas yields.

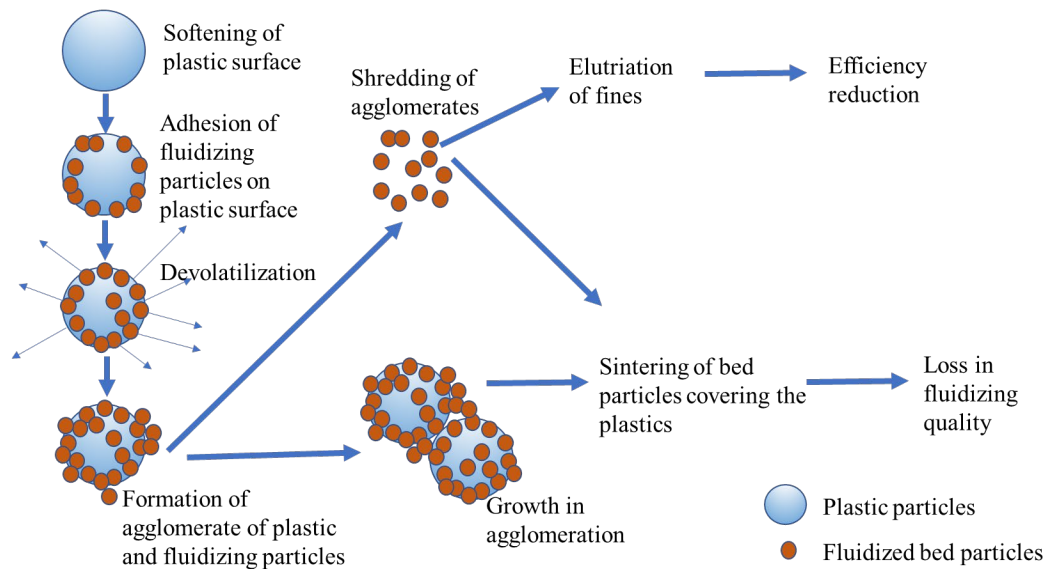


Figure 20. Difficulties in gasifying plastic particles in fluidized bed [65]

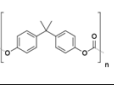
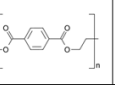
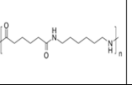
The above parallel benefits have motivated significant amount of research into co-pyrolysis and co-gasification which will be discussed here with the focus on the effect of feedstock composition [64,66–73]. While the influence of operational parameters such as temperature, pressure, heating rate, reactor type, catalyst and gasifier type is crucial for co-pyrolysis and co-gasification, their influence is similar to their effects during individual component pyrolysis and gasification [64]. This motivates us to focus on investigating the influence of blended feedstock content and their mixing method along with intimacy, whose effect on the product yield is non-trivial and non-additive, compared to pure feedstock conversion.

Chapter 2: Literature Survey

2.1 Introduction to co-processing of biomass with plastic and tire wastes

Significant literature is available that provides fundamental studies and reactor scale studies on co-pyrolysis and co-gasification of biomass/bio-waste with plastics, and other MSW wastes such as wet sewage sludge [66,71–76]. Since both pyrolysis and gasification involves pyrolytic decomposition as their starting point, fundamental studies on the reaction mechanism and kinetics involves understanding the influence of feedstock composition on the mechanism involved. Note that plastics are long chain hydrocarbon polymers as in polyethylene (PE), and polypropylene (PP) that may contain aromatic content as in polyethylene terephthalate (PET) and polystyrene (PS) used in bottling and packaging, and halogen content as in polyvinyl chloride (PVC) used for piping. Some characteristic plastics found in the waste and their heating value are given in Table 5. These materials have very high volatile content, and their degradation is preceded, coincided, or succeeded by melting or glass transition.

Table 5. Energy content and monomers of different types of plastics [77,78]

	HDPE and LDPE	Poly styrene	Poly carbonate	Poly propylene	Polyethylene terephthalate (PET)	Poly hexamethylene adipamide or Nylon	Poly methyl methacrylate (PMMA)	Polyvinyl chloride (PVC)
Estimated LHV (kJ/g)	44-47	41.96	30.32	42.66	23.22	28.76	25.1	20.5
Structure								
Uses	Containers, bags, film wraps	Packing peanuts, bottles	Windows, electronics, bottles	Piping, insulation	Textiles, containers	Textiles,	Glass alternative	Piping, cable insulation, construction

Fundamental studies on these biomass and plastics materials, both separately and as blends, involved micro scale reactor studies such as thermogravimetric analysis (TGA),

micro-pyrolysis which were sometimes equipped with the evolved gas analysis instruments, such as, mass spectroscopy (MS), gas chromatography (GC), and Fourier-Transform infrared spectroscopy (FTIR). The individual components studies revealed that polymers such as PE, PP, and PS provide approximately a single sharp TGA peak behavior corresponding to their decomposition [64]. In contrast, the plastics follow a free radical mechanism of decomposition involving radical formation from random scission followed by rearrangements and thermal cracking [79]. Low fixed carbon content in plastic wastes mean that majority of plastic wastes produce very low char. Hydrocarbon plastics such as PE and PP decompose via random scission leaving olefins as major products, which in parallel may rearrange into some aromatics as part of tar yield. The olefins during gasification can reform in the presence of H_2O , or CO_2 into H_2 , CO , and CO_2 or crack further to yield H_2 and CH_4 , depending on the temperature and catalyst present. Lack of carbonization pathway in these plastics mean that no char is produced from these plastics. Tar formation and its dependence on temperature and residence times in plastics is shown in Fig. 21 [55].

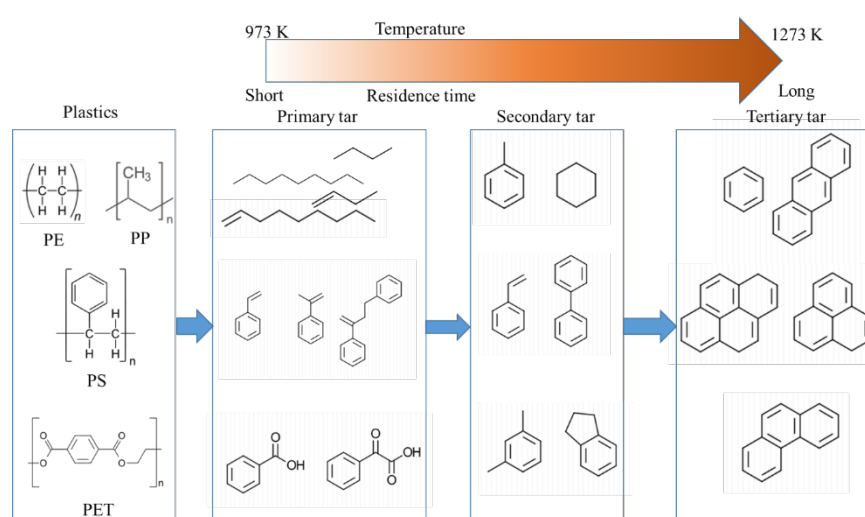


Figure 21. Tar formation from plastics during gasification [55]

Biomass decomposition using TGA peaks shows a complex decomposition behavior that predominantly involves two overlapping large peaks over a wide range. Such behavior corresponds to the complex structure of biomass involving cellulose, hemicellulose, and lignin. Majority of the biomass, that corresponds to energy production, is lignocellulosic and their behavior typically involves with drying around 373 K to remove absorbed moisture. Hemicellulose decomposes in the range of 463-563 K first due to its low thermal stability, followed by a narrow cellulose decomposition in 563-633 K due to its consistent monomeric structure. It is then followed by slow and broadband lignin decomposition over 633-773K due to its high stability that arises from its aromatic monomers and oligomers [80]. This process is called devolatilization, during which, the volatile materials escape the biomass leaving solid residue which carbonizes to form char. Note that the char yield can account for up to 30% by wt. of the product yield [37,41]. The inorganic content in biomass was also found to have influence on biomass decomposition by acting as catalyst to enhance the tar cracking during biomass gasification [37].

Biomass blended with plastics and rubber used for co-pyrolysis and co-gasification showed significant changes to the products yield and their composition. Synergistic and non-linear effects were also reported when biomass was co-gasified with plastics, which means that the product yields and compositions from co-processing of the blends were not a linear combination of the results from separate processing of the individual components at same respective mass under the same conditions. In the following sections, we investigate lab-scale observations and discussion on synergistic effects of co-processing biomass and plastic wastes with focus of its influence on product gas

characteristics with supporting data on bio-oil, tar and char characteristics. Initially we discuss the lab-scale and pilot scale macro-reactor studies that revealed the knowledge of synergistic effects and its possible outcomes with incorporating synthetic polymers. This will include co-gasification and co-pyrolysis studies with focus of its effects on product yield distribution and product gas characteristics. The review of this literature supported with appropriate discussion, will be followed by micro-scale studies of these mixture feedstocks and the effect of co-processing. This includes studies carried out using thermogravimetric analysis (TGA), pyrolysis-gas-chromatography/mass-spectroscopy (Py-GC/MS), TGA with evolved gas analysis using FTIR, MS or GC/MS and other micro-scale studies. Such a classification of investigations will provide us with the details of the missing knowledge with respect to the characteristics and potential of co-processing of biomass and plastic waste for syngas production.

Studies on co-gasification and co-pyrolysis carried out by converting the respectively chosen biomass and plastics separately and then comparing those results with the products produced from converting blends of those biomass and plastics for different mass ratios are useful to understand the influence of feedstock composition.

2.2. Macroscale findings of co-processing

For investigations into biomass blending with hydrocarbon polymers, we include literature on investigations into different types of PE (such as HDPE, LDPE, and MDPE), PP, waste tire and PS. As the investigations vary in their scale of operation, we first review the findings in the literature concerning the influence of addition of the above synthetic polymers to biomass wastes which will include components such as wood, agricultural and yard waste, and paper waste.

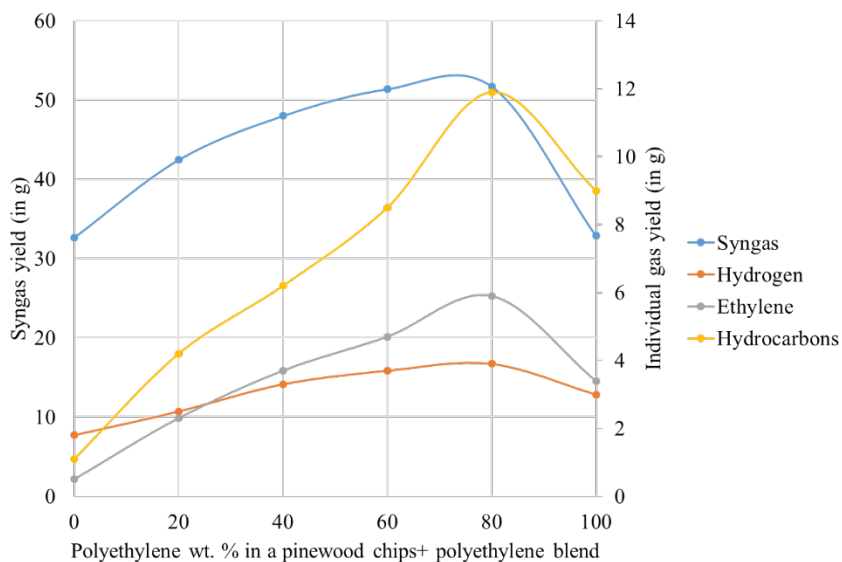


Figure 22. Synergy in the gaseous yields from steam gasification of pinewood and PE mixtures (mass: 35 g) [44]

Most commonly chosen biomass for these studies was pinewood while PE was the most commonly chosen hydrocarbon polymer [44,81–89]. Co-gasification of pinewood with PE in a steam rich lab-scale gasification reactor at 1173 K showed lowering of CO and CO₂ yield with increase in PE content [44]. This was due to lower oxygen content in PE and thus the net feedstock. Figure 22 shows that the presence of PE increased the yield of H₂, C₂H₄ and other hydrocarbon that enhanced the heating value of syngas produced based on this study [44]. While this was expected due to the change in C, H, O content in the feedstock and the type of bonds in the feedstock, another intriguing result was found. The syngas, H₂, and hydrocarbon yield from co-gasification of pinewood and PE was found to be higher than the weighted sum of yields when pinewood and PE were gasified separately. Although H₂ increased with increase in PE, this synergistic influence was not observed when pinewood was co-pyrolyzed with HDPE followed by inline catalytic steam reforming and suggesting reason being very

high H₂ yield by pyrolysis-inline catalytic reforming than steam gasification [90,91]. They report enhancement in conversion and H₂ concentration in syngas by catalytic steam reforming of the volatiles from co-pyrolysis instead of steam gasification. Figure 23 revealed similar results on mole fraction of gaseous species yield (CO, CO₂ and C₁, C₂, C₃ and C₄ hydrocarbons) during co-pyrolysis of beech-wood and PP [92].

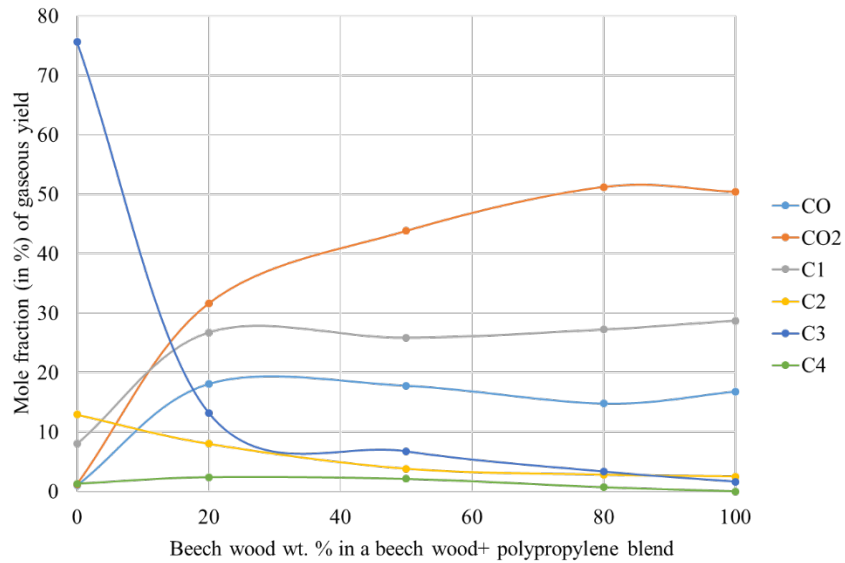


Figure 23. Effect of composition in beech wood and PP mixture on the gas yield composition [92]

Berrueco et al. found that gasifying PE with sawdust in a bubbling fluidized bed reactor yielded less tar and more gas yield from co-gasification compared to individual component gasification [93]. Moghadam et al. studied steam gasification of PE blends with palm kernel shells in catalytic fluidized bed to find that increasing PE content in the feedstock improved its conversion rate to syngas yield [85]. But this investigation lacked proper control on the biomass to PE ratio making it difficult to understand the possibility of synergy [85]. Gasification of high density polyethylene (HDPE) with pinewood in a conical spouted bed steam gasifier showed synergistic increase in gas

yields with simultaneous decrease in tar and char yield [90,94]. Arregi et al. found that the space time for equal conversion is 2.5 times lower with HDPE compared to biomass [90].

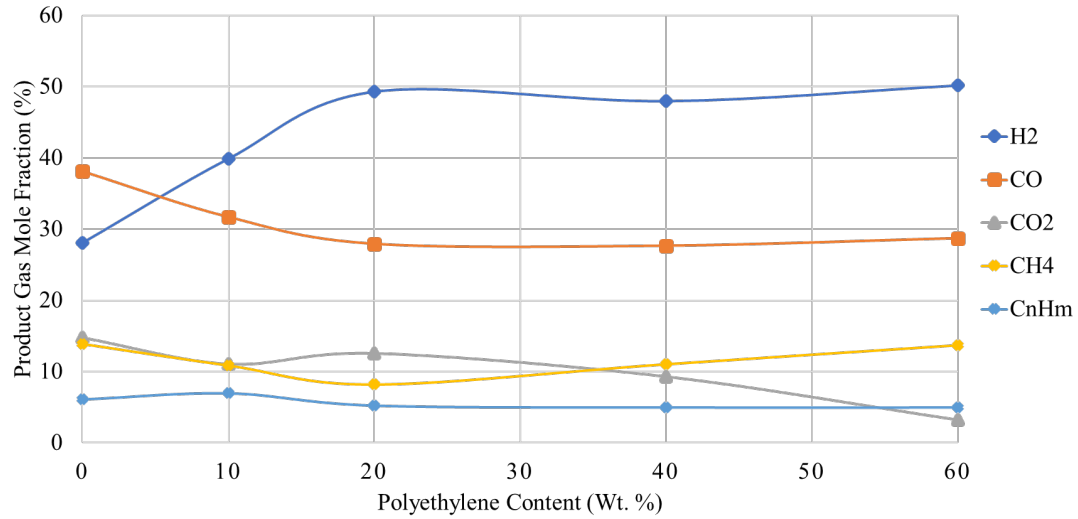


Figure 24. Synergistic variation in syngas composition with PE content in steam co-gasification of pinewood at 835 °C [70]

Pinto et al. carried out lab-scale continuously fed steam gasification of blends of pinewood and PE with varying composition in a to find an optimal blend ratio for pine wood in PE that resulted in maximum H₂ yield and this was due to favoring of reverse reactions, such as reverse water gas reaction, at high H₂ concentrations leading to an equilibrium which yielded H₂ max. of 50% in syngas, see Fig. 24 [70]. Similarly, optimal PE content in rice straw for high LHV of syngas with low tar yield was found by Yu et al. in entrained bed gasifier [95]. At higher temperature than 850 °C, Boudouard and water gas reactions dominate in their influence on the product yield leading to equilibrium driven output. This study reported that, gasification of feedstock containing only PE waste led to operational problems including softening of PE during

feeding which led to clogging (the situation didn't improve with cooling the feed or pelletizing), and the formation of black powder (coke) in large amounts in the reactor, the cyclone and the condensers [70]. This suggests that co-gasification is necessary not only for the improvement of biomass derived products but also enhance the utility of plastic wastes as gasification temperatures with plastic wastes alone leads to significant amounts of coke formation which is undesired due to its operational difficulty and loss of desired product yield. Addition of pinewood to PE was found to improve the operational control by avoiding the above issues. Similar improvement in co-gasification operation was found by Narobe et al. in dual fluidized bed 100 kW reactor in air, with plastic feeding issues resolved by co-feeding with biomass [96]. The synergistic interaction between PE and biomass does not always improve gas yields. Influence of heating rate, temperature and vapor residence time exists to control the effect of the interaction between PE and biomass on the relative yields of gas, liquid, and char yields. For example, in slow co-pyrolysis (10 K/min and 128 s vapor residence time) of cellulose and LDPE in fixed bed-reactor, co-pyrolysis resulted in synergistically lowering gas and solid yields while increasing the liquid yield [97]. Even though the relative yields of liquid and gas phase varied, the overall characteristics of interaction were positive, i.e., the HHV and thus energy recovery was synergistically enhanced in both the oil and char yields.

Co-processing of biomass with waste tire via gasification or pyrolysis can also alleviate the issues of fluctuations in the availability of biomass along with providing a net high calorific value and low O/C of the feedstock, which can improve the quality and quantity of syngas produced. It could also provide improved methods and pathways

to consume and utilize waste tire and biomass together at high conversion efficiency and better energy transformation. Previous studies report on the mixtures of waste tire and biomass using co-pyrolysis or co-gasification had limited focus on synergistic effect from the co-processing of different feedstocks on syngas yield during pyrolysis and gasification. Al-Rahbi et al. studied hydrogen-rich syngas production and tar removal from biomass gasification using char from tire pyrolysis as a catalyst for tar reduction and improving H₂ selectivity in a two stage fixed bed reactor [98]. Wang et al. investigated co-pyrolysis behaviors of biomass and tire at different (H/C_{eff}) ratios and found that hydrocarbon yields increased with increase in hydrogen/carbon ratio (H/C_{eff}) [99]. The optimal H/C_{eff} was determined considering the correspondingly higher yield of polycyclic aromatic hydrocarbons (PAH) and char residuals at higher percentage of waste tire. Some studies were focused on synergistic effect on liquid hydrocarbons yield while others focused on the fuel upgrading process [100–103]. Martínez et al. [100] carried out co-pyrolysis of forestry residues and waste tires and found positive effects between waste tire and biomass. Their studies showed that acidity, density, and oxygen content decreased, pH and calorific value increased with respect to the liquid yield from biomass pyrolysis, leading to upgraded bio-oil. This was linked to the presence of radical interactions between waste tires and products of biomass pyrolysis. The addition of waste tires to the feedstock blend significantly decreased the yield of aldehydes and phenolics in the liquid yield. Cao et al. [101] studied co-pyrolysis of wood biomass and waste tire with catalysts for improving liquid yield characteristics. Their results showed that co-pyrolysis favored inhibiting the formation of polycyclic aromatic hydrocarbons produced from tire while hydrogen

transfer and synergistic effects during co-pyrolysis of the biomass and tire improved the quality of the oil produced. Alvarez et al. [102] examined co-pyrolysis of pinewood sawdust and the waste rubber in order to improve the properties of bio-oil for its integration in oil refineries. Their results showed that addition of tire rubber improved the oil properties with higher carbon content and lower oxygen and water, but the sulfur content increased. Abnisa et al. [103] studied co-pyrolysis of palm shell and scrap tire and the effect of stepwise co-pyrolysis temperature to reveal that addition of scrap tire in the pyrolysis of biomass succinctly improved the quantity and quality of the liquid oil produced. The results showed that the addition of waste tires contributed to methane production, whereas wood biomass was favored to produce hydrogen. Co-pyrolysis of 50% biomass and 50% scrap tire was recommended for improved production of liquid and byproducts.

2.3. Microscale findings of co-processing

Different types of mechanisms of interaction were proposed to explain the synergy observed in lab-scale co-processing. This includes H-donor and radical stabilization provided by PE/PP, interaction between the radicals and volatile species, char from the biomass catalyzing PE decomposition, ash/inorganic content of biomass catalyzing PE decomposition. While these were proposed, lab-scale studies by direct co-processing is not sufficiently controlled to provide concrete understanding of this synergy. To understand these interaction effects that were observed on macro-scale, micro-scale studies were carried out and reported in the literature. One of the most used micro-scale study is the thermogravimetric analysis (TGA) which records the mass loss in the feedstock (~milligram) as the temperature increases linearly until complete

decomposition. Typical controlled heating rates in these experiments are 10-40 K/min. This is low heating rate compared to the lab-scale and industrial scale studies on gasification and fast-pyrolysis, but appropriate for slow pyrolysis. The product vapor that evolves during this non-isothermal decomposition were also analyzed in some studies using MS or FTIR to gain insight into the product evolution behavior.

In multiple TGA studies varying in the type of PE/PP used and the biomass used, the DTG (conversion rate with temperature/time) of the composite feedstock was found to be very close to a linear combination of the DTGs of individual solid components of the feedstock. Dong et al. also reported no apparent synergy in TGA results which showed the decomposition behavior of the blends to be a linear combination of the pure substances [84]. This could be from the slow heating rates in TGA studies which and lack of significant overlap between the biomass and plastic decomposition peaks leading to insignificant influence on each other's behavior. The non-additive effects could have arisen from interaction between the vapor/intermediate species of biomass and plastics among themselves and with the solid species of biomass and plastics during decomposition and it is possible that high heating rates are necessary. Indeed Dong et al. identified the non-additive synergistic behavior from evolved gas emissions which showed non-additive enhancement of hydrocarbon yield and reduction of CO yield [84]. Similar effects were found in gas composition at different conditions and different reactor designs for both pyrolysis and gasification, while relative gas, liquid and char yield varied with the conditions [69]. This could either mean there exist no solid-solid or solid-vapor interaction between biomass and PE or it could mean that TGA studies are not appropriate to understand the synergy obtained from co-pyrolysis or co-

gasification of biomass with PE. Even though the DTGs from co-pyrolysis showed no interaction, the net solid residue from co-pyrolysis was found to be synergistically lower than that from individual pyrolysis. It was suggested by Chen et al. to be an effect from secondary char cracking in the presence of PE to lower the char residue yield [104]. In some TGA studies on HDPE+cellulose mixtures, minor inhibition was also observed in the form of increased decomposition temperature of cellulose. This was reported to be possible due to HDPE melt covering cellulose and inhibiting its decomposition [105]. This shows that concrete knowledge of the influence of operating conditions including the usually unreported parameters such as heating rate, vapor residence times on the synergistic interaction between the feedstocks is lacking in the literature.

Other investigators have focused on the thermogravimetric behavior of biomass-waste-tire blends to determine their reaction kinetics [106,107]. Shi et al. [106] studied pyrolysis of fallen leaves and waste tires using thermogravimetric analyzer (TGA). The result showed three stages of thermal degradation for fallen leaves while it had only a single stage for waste tires. The co-pyrolysis of the two feedstocks provided a synergistic effect through radical interactions when compared to the pyrolysis of individual feedstock. Lahijani et al. [107] studied CO₂ assisted gasification of scrap tire and char (produced from palm empty fruit bunch and almond shell) at several blending ratios using isothermal TGA. Pure tire-char showed low reactivity that was attributed to mainly non-porous and graphitic structure. However, co-gasification of tire and almond shell or empty fruit bunch chars showed improved conversion at rates that was respectively 5 and 10 times higher than that from tire char.

The understanding of the contribution of different types of interaction such as solid-solid, solid-gas, liquid/melt-solid, liquid/melt-gas, and liquid-liquid is mostly missing in the literature on biomass and hydrocarbon polymer co-processing. One such study to resolve this was carried out using LDPE and cellulose co-pyrolysis using TGA and fixed-bed studies [97]. Pyrolyzing LDPE with char from cellulose (prepared at 400 °C and 550 °C) revealed that low-temperature char did not interact with LDPE according to TGA while the high temperature char catalyzed LDPE conversion to lower temperature decomposition as also reported by Jakab et al. using activated charcoal [97,108]. Liquid yield from pyrolyzing LDPE with cellulose char was higher by 7% (feedstock wt. basis) compared to predicted yield from combination of individual pyrolysis while co-pyrolysis of cellulose and LDPE had synergistic increase in liquid yield of 14%. Lowering of total char yield was also found by co-pyrolysis of cellulose with LDPE suggesting that char reacted with LDPE to increase in liquid yield while char underwent secondary cracking to lower its mass. To reportedly understand the influence of gas-gas, gas-liquid and liquid-liquid interaction or synergy during condensation, cellulose was pyrolyzed first in fixed bed reactor followed by cooling the reactor and removing cellulose char while retaining the liquid yield. This was followed by LDPE pyrolysis in the reactor which revealed a synergistic increase in the liquid yield suggesting the presence of synergistic interaction between the cellulose condensates and the LDPE vapors leading to rise in liquid yield. Combination of these two effects: synergy from char and synergy from condensates was found to be comparable to overall synergistic rise in liquid yield. While this paper provided the importance of mechanisms contribution in different phases, the results had low

dimension as only relative yields were investigated without the knowledge of composition of any of these phases and thus does not go far enough to provide concrete understanding of synergies in different phases.

Another type of micro-scale technique for investigation is micro-scale fast-pyrolysis with analysis of volatiles using GC-MS or FTIR studies. These reactors typically include milligrams of sample with heating rate of ~ 1000 K/s and in some cases also equipped with a downstream catalyst for volatiles reforming before direct heated volatiles analysis. Such analysis of cellulose and HDPE mixtures revealed that levoglucosan formation from cellulose has synergistically decreased in the presence of HDPE owing to proposed influence of H from beta-scission of HDPE [105]. HDPE also was found to favor decomposition of ketones, aldehydes, and acids from cellulose decomposition to form CO and CO₂ [105]. Alkane and alkene yield also increased synergistically in these mixtures. These results were supported by other similar studies including biomass with LDPE/HDPE mixtures [109,110]. It was also proposed that the oxygenates from biomass could promote the scission reactions in HDPE. From catalytic co-pyrolysis of cellulose with LDPE, it was also proposed that furans, that form from anhydrosugars of cellulose, and light olefins from LDPE decomposition undergo Diels-Alder reaction followed dehydration to form aromatics such as benzene, toluene, xylene (BTEX) [109]. Cellulose-PP studies also revealed vapor phase interaction which was proposed to be abstraction of OH radicals from cellulose to react with the hydrocarbon intermediates formed from chain-end beta scission and intramolecular H abstraction to form large amounts of alcohol products while simultaneously enhancing each other's pyrolysis reactions [111]. Co-pyrolysis of

mixtures of sugarcane bagasse with LDPE revealed lowering of O content and same was found in the case of walnut shell with HDPE showing also the improved C and H content in the bio-oil [82,112]. While these results showed clearer picture of products distribution, they lack in temporal data and account for overall products component yields.

TGA studies of rice straw with PET also revealed lowered activation energy by co-pyrolysis. Co-processing of biomass with polystyrene was also investigated in the literature [108,113–120]. Polystyrene (PS) is different from PE, and PP in terms of monomer composition containing benzyl ring. PS is a thermosetting polymer which means it is prepared by irreversible curing of its precursor by heating and thus formed PS cannot be melted to reshape once it is cured, unlike PP or PE which can be melted for molding into different shapes. This makes PS a more concerning issue in direct recycling compared to PE/PP and thus making its energy recovery the only viable pathway. Jakab et al. studied co-pyrolysis of polystyrene with charcoal and lignocellulosic materials and reported that poly-styrene had no impact on lignocellulosic pyrolysis while the char from lignocellulosic materials enhanced hydrogenation of the styrene monomer and other oligomers to increase the yields of hydrogenated aromatics, such as toluene and ethylbenzene [108]. Improvement to bio-oil quality and quantity was also observed by incorporating PS in pyrolysis of sargassum macroalgae [117]. TGA studies have also been carried out sometimes equipped with evolved gas analysis on co-pyrolysis of biomass with PS. Jakab et al. reported no influence of PS on biomass decomposition peak while biomass's presence delayed PS decomposition to higher temperature [108,121]. While the

GC/MS studies showed an increase in alkyl-aromatics and decrease in alkenyl aromatics with addition of these materials in the literature, the pathway for such impact remains unknown [108]. The release of alkenyl aromatics does not directly suggest this delay in polystyrene decomposition. A possible reason for the delay in PS decomposition during co-pyrolysis could be from improved stability of the oligomers formed during PS cleavage in the presence of char.

2.4 Knowledge gap and dissertation outline

While the synergistic effects were observed, the reason for such contributions is still debated. Suggestions for the reasons are as below. Some suggest the interaction between the plastic radical intermediates and the oxygenate volatiles of biomass. Others suggest that biomass decomposes earlier leading to biochar along with its alkaline metal content, which can act as catalyst to enhance the plastic component pyrolysis and its hydrocarbon cracking leading to enhanced H₂ yields and lower char yield. The reason for synergy could also be physical and not chemical, meaning that the plastic melt provides a different phase for biomass to decompose and the plastic melt could induce diffusion effects to influence the relative yields [122]. The inorganic content was suggested to be responsible for synergy via catalytic enhancement of thermal cracking which increases the gaseous yield. This clearly suggests the existence of a significant knowledge gap in the understanding of interaction between biomass and plastic components during gasification and its effects on the syngas produced along with its by-products. Investigation into the relative contributions from different interaction mechanisms such as solid-solid/melt interaction, solid-vapor, and vapor-vapor interaction is significantly lacking in the literature as no study is available to

appropriately concur the influence of each of these pathways on the synergy observed such as decreased char, increased gas yield and H_2 and light hydrocarbon yields when steam gasified.

This knowledge gap in the pursuit of efficient and sustainable gasifiers for biomass conversion and plastic wastes recovery motivates the present project and provides the pathway for the current investigations provided in the subsequent chapters.

Chapters 4-7 provide investigations carried out to understand and quantify the influence of interaction between different plastic wastes with biomass for different feedstock compositions, and gasifying environment. This will include pinewood, pine bark and paper waste as the biomass representatives and polypropylene, polyethylene terephthalate, polycarbonate, and polystyrene as the supplement feedstock representatives. These investigations will include the impact of feedstock composition, and gasifying agent (pyrolytic, steam gasification, and CO_2 gasification). As these reveal the synergy in process performance in macro-scale conditions. TGA modeling using distributed activation energy model (DAEM) was carried out to gain further insight into this interaction and its influence on the kinetic parameters, see Chapter 7.

While these studies reveal the impact of feedstock blending on its interaction behavior, the source of these interactions and their isolated influence on the process performance is not known. So, co-pyrolysis of pinewood with polypropylene, polycarbonate, and polystyrene was carried out using different feedstock arrangements to isolate these interactions and obtain their quantified influence on syngas evolution. These results are reported in Chapters 8-10 respectively. Based on these results on combined and delineated understanding of the interaction between different feedstocks during co-

pyrolysis and co-gasification, conclusions are made in Chapter 11 along with suggestions of future work that needs to be carried out to further this research into efficient utilization of sustainable reserves such as wastes and biomass for value-added products.

Chapter 3: Experimental Methodology

3.1 Introduction

This chapter provides the different experimental facilities, operating conditions, methodology of analysis and materials used for the experiments reported in this work. For macro-scale understanding, lab-scale semi-batch reactor equipped with product gas analysis was utilized. A series of feedstock arrangements were designed to provide a deconvoluted understanding of the synergistic interaction between feedstocks. Micro-scale kinetics were obtained using thermogravimetric analysis and their kinetic analysis was obtained using distributed activated energy model. The source, pre-processing, and properties of different biomass, and plastic utilized in this work are also provided.

3.2 Lab-scale Semi-batch Reactor

All the lab-scale fixed bed experiments on pyrolysis, gasification, co-pyrolysis, and co-gasification were carried out in the semi-batch reactor facility in the Combustion Lab at UMD. This facility is capable of isothermal investigations for temperatures to 1000 °C. The schematic of this fixed-bed semi-batch reactor that composed of a preheater and a main reactor is shown in Fig. 25. The batch reactor was named ‘semi’ because the reactant gases continuously flowed in and out of the reactor along with products while, for any given experiment, the solid reactant sample mass was introduced as a batch. The electric preheater furnace (Lindberg/Blue M Mini-Mite) was located directly upstream the main reactor and was used to ensure that the carrier gas enters the main reactor section at the desired set point temperature of the gas. The main reactor unit (Lindberg/Blue M 1200 °C Split hinge tube furnace) was an electrically heated

tube furnace of 45.7 cm length and 5 cm inner diameter. The preheater and main reactor temperatures were set at the same temperature and were electronically controlled by two external units that provided quasi-isothermal conditions inside the reactor. For the pyrolysis experiments only pure N₂ (99.998%) was passed through the reactor. In the case of CO₂ gasification, a mixture of pure N₂ and CO₂ (99.9%) were of controlled flow rates were used. But in the case of steam gasification experiments, a mixture of H₂ and O₂ were combusted in the presence of N₂ to obtain superheated steam with the controlled stream and N₂ flow rate. 2.1 sccm of N₂ was used for pyrolysis experiments, 2.1 sccm of total flow with 75% CO₂ and 25% N₂ was used for CO₂ gasification experiments. For steam gasification, 2.63 g/min of N₂ and 3.32 g/min of steam was used. The sample was placed in a stainless-steel cylindrical mesh and inserted into the main furnace via a quick disconnect coupling located at the end of the main reactor. A cylindrical tube made of quartz was used as the sample holder inside the mesh that allowed for easy sample introduction and char residue extraction from the reactor. The product gases evolved from the reaction chamber were passed through an ice bath condenser that removed moisture and tars. The sampling line was then split into two branches of sampling and bypass line. A micro GC (Agilent 3000A, USA) was calibrated to analyze the mole fractions of N₂, H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, and C₂H₆ in the evolved product gases with an accuracy of up to $\pm 0.1\%$. Most of the gas mixture was vented out through the bypass line while the sampling product gas stream after passing through two condensers was analyzed for gas composition using this gas chromatography. Since these thermochemical conversion processes of pyrolysis and gasification occur fast at high temperatures and the sampling time required for GC

analysis was approximately three minutes, gas sampling cylinders (total of 5) were used to collect gas samples at 0.5, 1, 2, 3 and 4 min, respectively from beginning of the experiments. These times were chosen based on previous literature using this facility for gasification and pyrolysis of different types of feedstocks [40,41,43,123]. After the first 5 min, the product gas was then sampled and analyzed online at the GC sampling rate. The overall amount of gas produced was calculated from a balance on the tracer gas (N_2), since both the constant flow rate of nitrogen fed into the reactor and its molar fraction in the gas stream analyzed by GC were known. From the known N_2 flow rate (used here as the tracer gas for internal calibration for the GC), the amounts of gases detected from the GC could be evaluated.

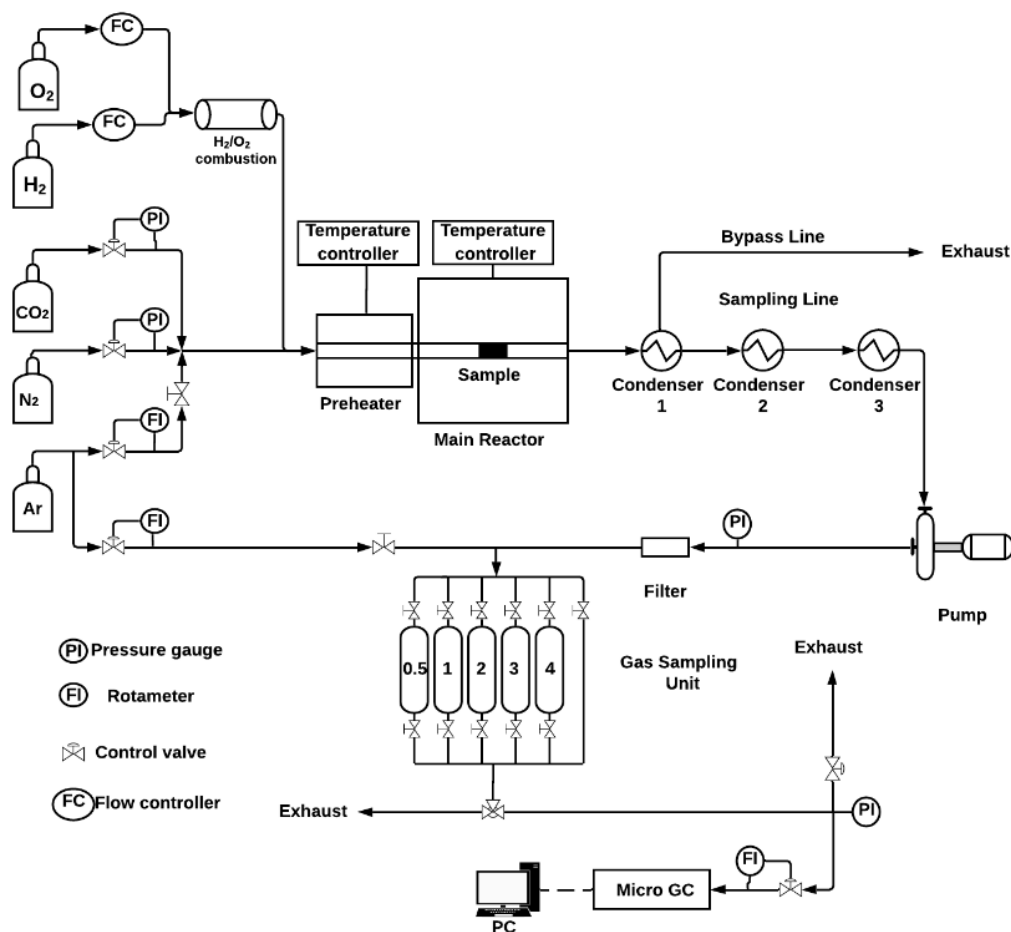


Figure 25. A schematic of the lab-scale fixed bed semi-batch reactor

Nitrogen was used in both pyrolysis and gasification experiments as a tracer and purge inert gas. Reactor, condenser, sampling unit and connection pipes were flushed with Argon gas prior to each experiment to make sure that the equipment was free from air and product gas residues from a previous run. The reactor conditions used for both pyrolysis and gasification tests along with the feedstock/feedstock mixture are stated in the respective chapters. While different temperature ranges were used in pyrolysis and gasification tests on pure feedstocks, co-processing experiments involving feedstock mixtures were carried out only at 1173 K to restrict our focus to understanding the synergistic effects on syngas behavior caused by feedstock

interactions. This temperature was chosen as both CO₂ and steam gasification are active at this temperature with sufficient thermodynamic equilibrium drive while pyrolysis at in these conditions also favors syngas formation. The flow rate of N₂ in pyrolysis and N₂+CO₂ mixture in gasification was chosen to maintain the same vapor residence time and appropriate to obtain better syngas yield while providing temporal variation of the syngas detected by the GC.

3.3 Feedstock Arrangement

From the previous chapter reviewing literature survey, we understand the significant gap in the knowledge concerning the utilization of biomass-plastic mixtures for syngas production via co-gasification. While the synergy was observed in the form of enhanced syngas yield, increased H₂, enhanced bio-oil yield and quality, lowered liquid oxygenates and increased CO and CO₂ yields, mutually enhanced kinetics, and increased heating value of the products in most of the biomass-plastic mixtures when co-gasified in lab-scale reactors. To understand the mechanism of this synergistic interaction, micro-scale studies were carried out in the literature using TGA, Py-GCMS or Py-FTIR and other similar studies. While these provided more insight into the behavior at different controlled heating rates and the influence of mixtures on all the volatiles and gases yields, these studies on their own do not provide complete picture and physical aspects of mechanism of interaction.

Along with that, a scientific strategy towards understanding the mechanism of interaction between biomass and plastics and its effect on the product characteristics is still lacking. The result of this missing intent to use scientific strategy has led to

significant amounts of studies in the literature using various types of biomass and plastics and using various reactors but of similar nature studies with no new concrete evidence of step-by-step interaction. One of the missing features of synergistic studies in the literature was insight into the contribution of synergy at various interphase and intra-phase interactions such as biomass solid-plastic solid, solid-vapor, vapor-vapor reactions, and reforming reactions on the final synergistic syngas yield and composition. In addition to this, the mechanism of solid-solid interaction is also missing in the literature along with its significance towards the synergy reported in macro-scale reactors.

This project will focus on these gaps in the knowledge on synergistic effects in product gas characteristics via co-gasification of biomass-plastic wastes. We try to address these gaps using various methods to obtain the interaction at each physical aspect of co-gasification to obtain their respective contributions to the overall synergy reported in the literature. This will include micro and macro-scale studies with modified reactors to focus on individual aspects of interaction. Products will be characterized and quantified for their yield, kinetics, and composition to understand the chemistry of these interactions.

3.2 Modified reactors for physical insight into synergistic interaction

In the literature, synergistic behavior in product gas characteristics was proposed to be from various mechanisms which include: biomass char and ash interaction with plastics to vary plastics decomposition, presence of plastics improving or inhibiting biomass pyrolysis, vapor-vapor interaction between H abstraction, olefins and aromatics from the plastics and the oxygenates such as furan and phenols from

biomass, the change in relative yields of the product gases from pyrolysis providing synergistic influence on the product gas after gasification/reforming. While these different methods were proposed their individual contributions were not reported in the literature. In this project, we try to address this issue by deconvoluting each of these pathways of interaction by modifying small lab-scale reactor to provide only one of the interaction pathways mentioned above while avoiding other pathways of interaction.

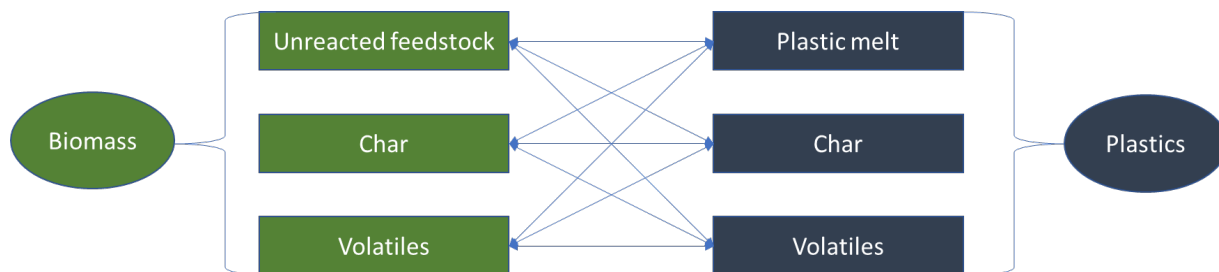


Figure 26. Simplified intermediate groups to understand synergistic interaction in co-pyrolysis of biomass and plastics

Co-pyrolysis and co-gasification experiments in the lab-scale reactor were carried out using different feedstock arrangements in the sample holder. Deconvoluted pathways possible from synergistic interactions during co-pyrolysis of biomass and plastics are depicted in Fig. 26. Here, we consider that the various interactions involving biomass-volatiles and plastic-volatiles, volatiles and solid feedstocks, volatiles and chars, and solid feedstocks and chars could all contribute to the overall synergy. Moreover, these interactions may occur both chemically and physically. The chemical interactions during co-pyrolysis could result from the variations in element composition and chemical bonds of different feedstocks, while the physical interactions are mainly ascribed to the thermal-softening or melting of the plastics. Note that some plastics which undergoes transition from amorphous to viscous melt phase before the

start of degradation. Since polymer in its melt state is characterized by low heat transfer rate and weak diffusion capacity [124,125], this melt state considered here may act as a physical barrier to heat and mass transfer during the co-pyrolysis process. Such complex physical and chemical interactions make it difficult to elucidate the detailed synergistic mechanism via the evenly mixed co-pyrolysis scenario. We designed some distinct feedstock configurations to clarify the separate contributions of volatiles and chars in the overall synergy. This deconvoluted understanding is expected to provide more insights into the synergistic behaviors and the underlying synergistic pathways in co-pyrolysis of biomass and plastics.

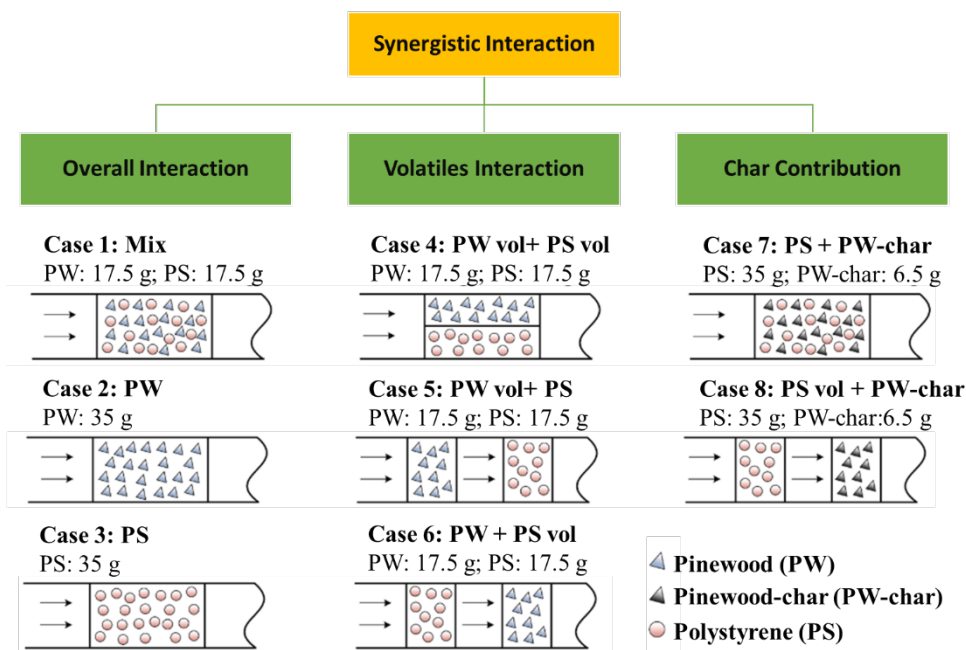


Figure 27. Different cases of feedstock arrangement for deconvolution of synergy in co-pyrolysis (Ex:pinewood-polystyrene)

The details of a typical tailored set of feedstock configurations are shown in Fig. 27.

The co-pyrolysis cases reported here were performed at 900 °C with 1:1 mass ratio of

biomass and plastics. But for the Case 1 of evenly mixed feedstocks, we also carried out co-pyrolysis and co-gasification experiments with different biomass to plastic mixture ratios to understand its effects. These tailored experiments were carried out for different types of plastic wastes mixed with biomass and the specific operational conditions will be provided in its respective chapters. Cases 1-3 were arranged to quantify the extent of synergistic effects. Specifically, Case 1 (denoted as Mix) was the co-pyrolysis case with evenly mixed configuration, wherein the possible synergistic interactions shown in Fig. 26 were all included. Cases 2 and 3 were the pyrolysis of biomass and plastics as individual feedstocks, which represented as the baseline cases to help identify the possible synergistic effects in co-pyrolysis.

Case 4-6 were designed to evaluate the contributions of volatiles interactions to the overall synergy during co-pyrolysis. In case 4, a thin quartz plate was used to separate the feedstocks with half of the cross section filled with biomass and the other half filled with plastics. With this configuration, only the mutual interactions between biomass-volatiles and plastics-volatiles (purged downstream of the sample position by the N_2) were involved while the other possible interactions shown in Fig. 26 were all excluded. In case 5, the feedstocks were separated with plastics placed downstream to investigate the effects of biomass-volatiles on plastics degradation. For case 5, in addition to volatiles mutual interactions, the interactions between biomass-volatiles and unreacted solid plastics (or plastics' melt state) were also included. Similarly, the separated configuration with biomass placed downstream was employed in case 6 to examine the effects of plastics-volatiles on biomass decomposition, which involved the volatiles

mutual interactions, catalytic influence of bio-char on plastics-volatiles and the interactions between plastics-volatiles and unreacted solid biomass.

Cases 7 and 8 were deployed to understand the roles of bio-char and plastics-char in co-pyrolysis. In some cases, plastics do not form char, and these will be discussed later. Case 7 involved the pyrolysis of plastics in the presence of bio-char and Case 8 considered to separate plastics from bio-char to avoid direct contact. These two cases are expected to provide information on the effect of char from either feedstocks on each other's decomposition. Note that char used here was prepared from the individual pyrolysis of biomass and plastics at 900 °C for 21min, which was the same condition as that of co-pyrolysis of biomass-plastics mixture. The amount of char used here was determined based on the mass ratio of biomass to plastics at 1:1 after the mass of char was converted to that of original feedstock.

3.4 Species' mass flow rate calculation

The mass flow rates of evolving product species from the lab-scale fixed bed reactor experiments were obtained using their respective mole fractions obtained from the GC analysis at different times, as mentioned above, during the experiments. Specific to this subsection, below is the nomenclature of the variables used.

$m_{CO_2}^i$	Mass flow rate of CO ₂ at the reactor inlet
$m_{N_2}^i$	Mass flow rate of N ₂ at the reactor inlet
$m_{H_2}^f$	Mass flow rate of H ₂ at the reactor outlet
m_{CO}^f	Mass flow rate of CO at the reactor outlet

$\dot{m}_{CH_4}^f$	Mass flow rate of CH ₄ at the reactor outlet
$\dot{m}_{UG}^f$	Mass flow rate of unknown/undetected gases at the reactor outlet
$\dot{m}_{UL}^f$	Mass flow rate of unknown liquids (tars) at the reactor outlet
$\dot{m}_{CO_2}^f$	Mass flow rate of CO ₂ at the reactor outlet
$\dot{m}_{N_2}^f$	Mass flow rate of N ₂ at the reactor outlet
k	Portion of gas flow sent for GC sampling
Δt	Time duration of gas sample collection by gas sampling valve in the GC
r_i	Response factor of gas
A_i	Area of gas species i measured by thermal conductivity detector (TCD) in the GC
$\dot{V}_{N_2}^i$	Standard volumetric flow rate of N ₂ at NTP
ρ_{N_2}	Standard density of N ₂ at NTP
ρ_i	Standard density of gas species i at NTP
Mw _i	Molecular mass of species i
$\langle \dot{m}_i^f \rangle$	Average mass flow rate of i th species over time duration Δt

To explain the methodology of calculation of product gas flow rates, yields and mole fractions from the GC raw data, a simplified example reactor setup similar to the present one has been used in the Fig. 28 below.

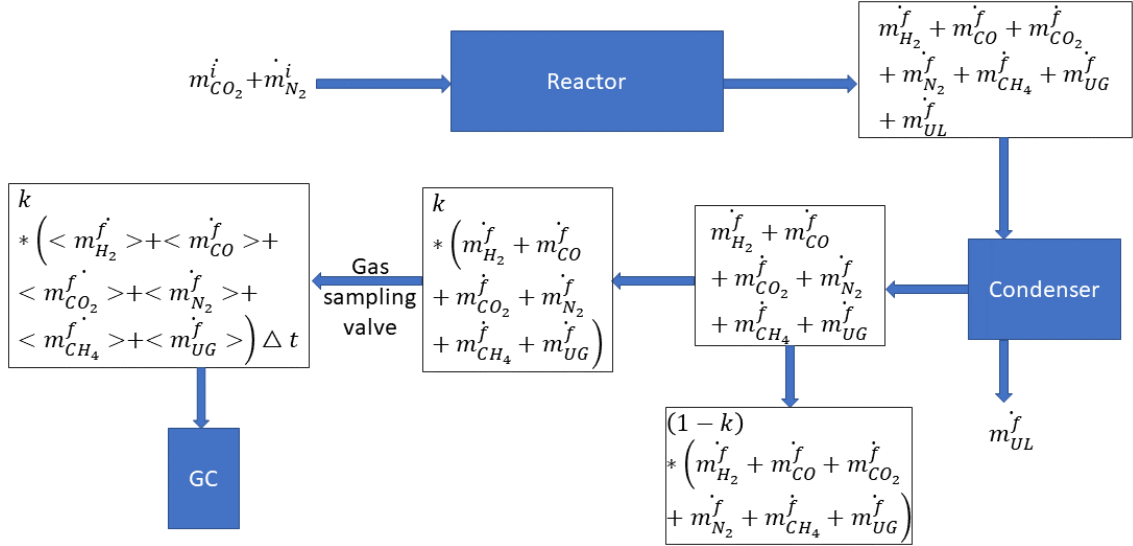


Figure 28. Formulated schematic of the experimental setup to show data processing

In the above example, N_2 and CO_2 , at a predetermined gas flow rate, are sent into the reactor where it reacts with a solid, decomposing sample resulting in a gaseous mixture of H_2 , CO , CO_2 , CH_4 , N_2 and other unknown gases (UG) and volatiles which cool down to form liquids (UL) at room temperature. The main but reasonable assumption to this formulation is that N_2 does not react in the reactor. Thus, $m_{N_2}^f = m_{N_2}^i$ during the reaction. This gas mixture was condensed and thus separating the unknown liquids from the mixture. Following this, the gas mixture contained H_2 , CO , CO_2 , CH_4 , N_2 , and UG. A portion of this gas mixture was sent for analysis in the gas chromatogram (GC) equipped with thermal conductivity detector (TCD) while the rest of the gas was vented. Assuming the gases were fully mixed, each of the gas species are divided similarly. Thus, k portion of the gas goes to the GC while $1-k$ is vented. The GC is equipped with gas sampling valve which collects a portion of the gas mixture from the flow for a specified time duration (Δt), called sampling time duration. So, $k * \left(\dot{m}_{H_2}^f + \dot{m}_{CO}^f + \dot{m}_{CO_2}^f + \dot{m}_{N_2}^f + \dot{m}_{CH_4}^f + \dot{m}_{UG}^f \right) \Delta t$, is the

gas sample that goes into the GC columns for chromatographic separation. Note that, while the GC is collecting the gas sample, the molar flow rate of individual species changes and thus the mole fraction. So, for each gas sample, mole fractions analyzed by the GC, are average mole fractions over the period of Δt . Thus, the any data obtained and analyzed is an average over time duration of Δt , making it the minimum uncertainty in the temporal resolution of the data. After each of the detectable gas species are separated, their volume was measured using the TCD and calibrated using calibration gas which provides response factor of ' r_i ' for gas species i . Equation (2) shows the relation between the volume of species H_2 , for example, measured by the GC with respect to the mass flow rate of individual components of the gas mixture sample. In Eq. (2) V is the volume of gas analyzed by the GC, and X_{H_2} is the mole fraction of H_2 in that gas sample as measured by the GC. Now, taking the ratio of the mole fractions measured by the GC with respect to N_2 which yields Eq. (3) providing mass flow rate of H_2 and considering the mass flow rate of N_2 does not change with time. Equation (4) finally provides the relation between mass flow rate of H_2 (at time t averaged over the range $[t, t+\Delta t]$) and the input flow rate of N_2 , considering ideal gas equation which provides $\rho_{N_2} * \frac{Mw_{H_2}}{Mw_{N_2}} = \rho_{H_2}$. During the Δt , the chemical reactions lead to change in the number of moles so that the treatment applied here provides only a simplified approximation on the values of the reaction data. And thus, it leads to $\langle \dot{m}_{H_2}^f \rangle = \frac{X_{H_2}}{X_{N_2}} * V_{N_2}^i * \rho_{H_2}$ as in equation $M_i = \frac{X_i}{X_{N_2}} * V_{N_2} * \rho_i$ given in the manuscript.

$V * X_{H_2} = \frac{V * k * \Delta t * \langle \dot{m}_{H_2}^f \rangle / Mw_{H_2}}{k * \left(\frac{\langle \dot{m}_{H_2}^f \rangle}{Mw_{H_2}} + \frac{\langle \dot{m}_{CO}^f \rangle}{Mw_{CO}} + \frac{\langle \dot{m}_{CO_2}^f \rangle}{Mw_{CO_2}} + \frac{\langle \dot{m}_{N_2}^f \rangle}{Mw_{N_2}} + \frac{\langle \dot{m}_{CH_4}^f \rangle}{Mw_{CH_4}} + \frac{\langle \dot{m}_{UG}^f \rangle}{Mw_{UG}} \right) \Delta t} = r_{H_2} * A_{H_2} .$	(2)
$\frac{\langle \dot{m}_{H_2}^f \rangle}{Mw_{H_2}} = \frac{r_{H_2} * A_{H_2}}{r_{N_2} * A_{N_2}} * \frac{\langle \dot{m}_{N_2}^f \rangle}{Mw_{N_2}} = \frac{r_{H_2} * A_{H_2}}{r_{N_2} * A_{N_2}} * \frac{\dot{m}_{N_2}^f}{Mw_{N_2}}$	(3)
$\langle \dot{m}_{H_2}^f \rangle = \frac{r_{H_2} * A_{H_2}}{r_{N_2} * A_{N_2}} * \dot{m}_{N_2} * \frac{Mw_{H_2}}{Mw_{N_2}} = \frac{X_{H_2}}{X_{N_2}} * V_{N_2}^i * \rho_{N_2} * \frac{Mw_{H_2}}{Mw_{N_2}} = \frac{X_{H_2}}{X_{N_2}} * V_{N_2}^i * \rho_{H_2}$	(4)

3.4 Extent of synergy (weighted calculation)

The extent of synergistic effects was evaluated from a direct comparison between the results from co-pyrolysis/co-gasification of biomass-plastics mixture with the corresponding weighted average values from pyrolysis/gasification of individual components, as shown in Eq. (5) and Eq. (6). Here Y_{biomass} , Y_{plastics} , Y_{mix} represent the experimental values (gas flow rate and yield, energy yield, char yield, mass-loss conversion, or other parameters) from individual biomass pyrolysis, individual plastics pyrolysis, and co-pyrolysis of evenly mixed biomass-plastics mixture, respectively, Y_{weighted} the weighted average values based on Eq. (5), α the mass fraction of biomass in the mixed feedstock, and ΔY the extent of synergistic effects. So, for the all the synergy exposition in this dissertation this is the methodology of calculating weighted results.

$$Y_{\text{weighted}} = \alpha Y_{\text{biomass}} + (1 - \alpha) Y_{\text{plastics}} \quad (5)$$

$$\Delta Y = \frac{Y_{\text{mix}} - Y_{\text{weighted}}}{Y_{\text{weighted}}} \quad (6)$$

3.4 Thermogravimetric analysis

Pyrolytic breakdown of all the feedstock used in the experiments was examined using thermogravimetric analysis (TGA) in a TA Instruments SDT Q600 with horizontal balance, which was equipped for simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA-DSC). For all the investigations 1-10 mg of sample was used. The sample was dried at isothermal conditions of 383 K for 10 min in the TGA before ramping to higher temperatures. Chemically pure argon at 100 sccm flowrate was used as the purge gas for all the experiments. Experiments were conducted in an alumina pan, wherein a thin layer of the sample was laid for even reaction kinetics. Different blends of biomass and plastic mixtures were heated from 383 K to 1223 K at constant heating rates of 10 K.min⁻¹. To understand the influence of ramp rate, pyrolysis of individual components at different heating rates of 10 K.min⁻¹, 20 K.min⁻¹, and 30 K.min⁻¹ were also conducted. For different tests conducted, different heating rates were utilized and will be stated explicitly during the results discussion. Multiple runs were carried out by changing the way of mixing biomass with plastics to eliminate the influence of mixing on the co-pyrolysis kinetics. Since the feedstock particle size was less than 100 µm, the effect of size and diffusion limitations on the kinetics were negligible so that the measured kinetics corresponded to the actual chemical kinetics.

3.5 Distributed Activated Energy Model (DAEM)

To understand the interaction between biomass and plastic wastes in a TGA environment distributed activated energy model (DAEM) was utilized. This model is a lumped kinetic model, which was formulated as decomposition via large number of parallel and mutually exclusive reactions represented by a continuous distribution of activation energy and same frequency factor for each set of reactions. Conversion (α), in Eq. (7), can be represented by the aggregate from the set of parallel reactions in Eq. (8), whose activation energy distribution is $F(E)$; R being universal gas constant, k_0 – frequency factor, T – temperature, β – heating rate, and E – activation energy. Here, we fit the experimental DTG (differential thermogravimetry), or the rate of conversion with temperature ($d\alpha/dT$) represented in Eq. (9) which is appropriate for the representation of characteristics of feedstock decomposition. Equation (8,9) correspond to the assumption of 1st order reactions which is appropriate for the materials used. Generic n^{th} order formulation of DAEM can be found in ref. [126]. DAEM based DTG as in Eq. (9) represents set of reactions for decomposition of single component i . In the literature, lignocellulosic biomass is represented by the weighted sum of three sets of reactions ($n=3$) each of whom is governed by its own frequency factor k_i , and activation energy distribution $F_i(E)$ weighed by w_i as in Eq. (10), but for plastic waste pyrolysis, a maximum of two components are sufficient for accurate representation. So, for the blends of biomass and plastic wastes, each of the tests are fit to a five component model with each component represented by a Gaussian distribution for activation energy controlled by two parameters E_{oi} and σ_i , and frequency factor k_i as in Eq. (11). As in Eq. (10), for a five component model, $n=5$ and weights w_i ($i=1,2, \dots, 5$). These weights

are normalized so that the constraint in Eq. (12) is valid to maintain that the five components add up to the total/ feedstock decomposition.

$$\alpha(T) = \frac{m(T) - m(T_o)}{m(T_f) - m(T_o)} \quad (7)$$

$$\alpha_i(T | k_i, F_i(E)) = 1 - \int_0^\infty \exp\left(-\int_{T_o}^T \frac{k_i}{\beta} \exp\left(-\frac{E^*}{Rt}\right) dt\right) F_i(E^*) dE^* \quad (8)$$

$$\frac{d\alpha_i(T | k_i, F_i(E))}{dT} = \int_0^\infty \frac{k_i}{\beta} \exp\left(-\frac{E^*}{RT} - \int_{T_o}^T \frac{k_i}{\beta} \exp\left(-\frac{E^*}{Rt}\right) dt\right) F_i(E^*) dE^* \quad (9)$$

$$\frac{d\alpha_{sample}(T)}{dT} = \sum_{i=1}^n w_i \frac{d\alpha_i(T)}{dT} \quad (10)$$

$$F_i(E | E_{oi}, \sigma_i) = \frac{1}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{(E - E_{oi})^2}{2\sigma_i^2}\right) \quad (11)$$

$$\sum_{i=1}^n w_i = 1 \quad (12)$$

$$Obj(k_i, E_{oi}, \sigma_i) = 100 \left(\frac{dT}{d\alpha}\right)_m \sqrt{\frac{\sum_{p=1}^{n_p} \left[\frac{d\alpha_i(T | k_i, E_{oi}, \sigma_i)}{dT} - \left(\frac{d\alpha_i(T)}{dT}\right)_{ex} \right]^2}{n_p}} \quad (13)$$

To evaluate the experimental $d\alpha/dT$ ($(d\alpha/dT)_{ex}$), $m(T_f)$ was chosen to be the mass at 1173 K from the TGA results while $m(T_o)$ was chosen to be the mass of sample after drying for 10 min at 383 K. To obtain the corresponding parameters for a 5 component DAEM at each of the examined conditions, the objective parameter as in Eq. (13) was minimized. The complexity of this objective function due to its discrete and non-linear nature requires an efficient minimization algorithm for this single objective, and single constraint problem. Non-dominated sorting genetic algorithm (NSGA-II) was used for

this constrained minimization [127]. Bounds of the model parameters were set to $E_{oi} \in [100, 400]$ kJ/mol, $\sigma_i \in [0, 50]$ kJ/mol, and $k_o \in [10^{10}, 10^{20}]$ s⁻¹ and $w_i \in [0, 1]$ along with constraint as in Eq. (12). Maximum population of 700 and generations of 400 were required in certain cases to minimize the objective function below 4%. The parameters obtained corresponded to normalized objective function minimized to less than 4%. Since this function also represents the average deviation of the model from experimental values as used in ref. [128], the max. error from these model parameters was less than 4%.

3.5 Feedstock Materials

Table 6. Proximate and ultimate analysis of all the feedstocks along with their respective heating values

	Ultimate analysis (wt.%) ^a					Proximate analysis (wt.%)				LHV (MJ/kg)
	C	H	N	S	O ^c	Moisture	Ash	Volatile	Fixed carbon	
Pinewood	48.72	6.52	0.23	0.12	44.41	0.0	0.2	85.6	14.2	17.65
Paper Waste	41.5	6.4	0	0.0	51.9	0.0	6.7	82.3	11.0	14.06
Pine bark	50.4	4.2	1.6	0.0	43.8	5.2	4.8	63.9	26.2	18.8
Polypropylene	85.6	13.8	0	0	0.6	0.0	0	99.5	0.5	40.15
Polystyrene	92.0	8.0	0	0.04	0	0.0	0.0	99.9	0.1	42.75
Polycarbonate	75.3	5.5	0	0	19.1	0.0	0.0	79.4	20.6	25.51
PET	62.8	4.3	.07	.04	32.8	0.0	0.0	88.0	12	22.8*

^a Dry ash free basis

^c Calculated by difference

*High heating value

3.5.1 Pinewood

The pinewood pellets were obtained from Drax Biomass, having a characteristic size of around 8 mm (diameter) $\times$ 12 mm (length). All the samples were dried at 105 °C for 8 h prior to their use. Ultimate analyses, proximate analyses, and lower heating values (LHV) of pinewood are reported in Table 6 along with other feedstocks. These characterization studies of pinewood were carried out using elemental analyzer (Vario EL cube, Germany), proximate analyzer (UV-02053-00, USA), and rapid calorimeter (5E-KCIII, China) based on China's National Standard GB/T 31391, GB/T 212, and GB/T 213, respectively [129]. The characterization studies of pinewood were repeated 2 times and the average values were reported in Table 6 with standard deviation within 2.5%.

3.5.2 Paper Waste

Shredded clean office copier paper was used for paper waste in the experiments. A typical set of proximate, and ultimate analysis with lower heating value are provided in Table 6 from the literature [11].

3.5.3 Pine bark

Samples of pine bark were obtained from a plant nursery. The pine bark was grounded to obtain 140 mesh particle size (0.105mm) for thermogravimetric analysis. The pine bark was cut to a size of approximately 1.5 cm $\times$ 1 cm for the fixed bed experiments. The proximate, elemental analysis and gross calorific value of pine bark are listed in Table 6. Proximate analysis was carried out using TGA according to ASTM 7582-15 methodology [130], while the rest were obtained using similar method to pinewood.

3.5.4 Polypropylene

Polypropylene with average molar weight of ~250 kg/mol was obtained from Sigma-Aldrich as the plastic feedstock. In the case of steam co-gasification experiments post-consumer recycled polypropylene pellet-beads were used. Due to the uniformity of the plastic wastes a typical set of proximate, and ultimate analysis with lower heating value are provided in Table 6 obtained from the literature [11,77,78].

3.5.5 Polystyrene

Polystyrene used (obtained from Sigma-Aldrich) was in the form of beads with molecular weight ~192,000 g. Due to the uniformity of the plastic wastes a typical set of proximate, and ultimate analysis with lower heating value are provided in Table 6 obtained from the literature [11].

3.5.6 Polycarbonate

Bisphenol A polycarbonate (obtained from Sigma-Aldrich) was also in the form of pellets with a characteristic size of 2 mm (diameter) × 4 mm (length) and weight-average-molecular weight (Mw) of 45000 g/mol. In the case of steam co-gasification experiments post-consumer recycled black-polycarbonate (BPC) pellet-beads were used. The data for polycarbonate were obtained from the literature as these characteristics in plastic wastes are expected to be uniform, see Table 6 [131].

3.5.7 Polyethylene terephthalate

Polyethylene terephthalate was used only for steam co-gasification experiments and this was in post-consumer recycled flake form. The data for polyethylene terephthalate were obtained from the literature as these characteristics in plastic wastes are expected to be uniform, see Table 6 [11,131].

Chapter 4: Synergistic effects in steam co-gasification of biomass-different plastic waste components

4.1 Introduction

Plastic wastes contain different types of polymers having low and high density materials, such as, polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET/PETE), polyvinyl chloride (PVC), polystyrene (PS), polycarbonate (PC). Although each of these polymers have different monomer composition with different carbon, oxygen and ash content, the common feature among plastic waste is the high volatile content, high viscosity with low melting points and high energy density due to very low moisture and ash content [132]. Investigations found that catalytic or synergistic effects in co-gasification and co-pyrolysis with radicals released by one component enhanced the decomposition of the other component in the feedstock [44,83,119,133]. Biomass and plastics comprise of different monomers; an emphasis on decomposition of these in the presence of each other is necessary to further understand their important role. The effect of the composition, H/C and O/C of the monomers involved can help one to better understand this non-linear interaction. In this chapter, we examine gasification of biomass with different but homogeneous plastics in the presence of steam to understand the effect of different monomers of plastics to enhance or deteriorate the product gas yields.

This chapter provides results on the isothermal gasification of different compositions of 100% pine wood pellets in the presence of three different types of plastics at 1173 K using steam as the gasification medium. Plastics in the amounts of

0, 60, 80, 100% were mixed with biomass. Three different kinds of plastics examined here were polypropylene (PP), black polycarbonate (BPC), polyethylene terephthalate (PET). All these plastics were post-consumer recycled with PP and BPC being pellet extrudes while PET being small size flakes. The experiments included lab-scale steam gasification studies at 900 °C with a tracer gas flow of 2.63 g-min⁻¹ of N₂ and a steam flow of 3.32 g-min⁻¹, in addition to TGA examination of these mixtures. These plastic wastes were chosen as they provided different oxygen content and heating value along with different monomer structure of plastics. Mixture fractions of 0, 60, 80 and 100% plastics in biomass were used. The experiments were carried out until no product gas yield was evolved and no significant char residue left. The tar yield was not considered since the focus here was on syngas product yield.

4.2 Results and Discussion

Experimental data obtained using gas chromatography were processed to obtain volumetric composition of the different components present in the dry gas yields. The mass flowrates of the species were calculated with respect to known flowrate of N₂ which were integrated over the measured reaction time to obtain cumulative yields of different gaseous species. The cumulative yields from the mixture of biomass-plastic feedstocks (blue line in the graphs) were compared with weighted sum of yields when gasified individually (green line in the graphs) with weighted means the mass of biomass and plastics in the mixture to understand the extent of synergistic interaction due to two different components in the feedstock.

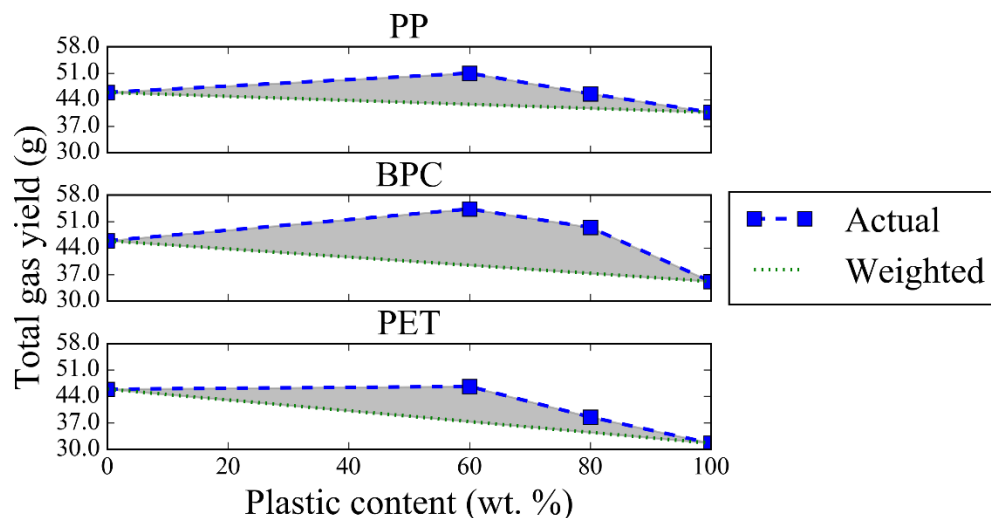


Figure 29. Comparison of cumulative total product gas yields for different plastic/biomass ratios using PP, BPC, and PET plastics.

Figure 29 reveals the synergetic enhancement of net gaseous yields using biomass-plastic mixtures. The comparison shows that co-gasification of plastics and biomass yielded enhanced solid feedstock to gaseous conversion compared to gasification of either the biomass or plastics as individual components. The use of only 60 and 80% plastic contents for comparison was based on the results obtained for co-gasification of wood-chips and polyethylene as in ref. [44]. This means that the interaction existed irrespective of the monomeric composition of the plastics used. Devolatilization of biomass started before radical formation in plastics. The volatiles can help in the radical forming reactions leading to enhanced lighter molecules yield and better conversion to gaseous products. Significant synergistic enhancement in gaseous yield was observed, especially for 60% ratio, and it was consistent for all the plastic types examined here. Although this figure shows enhancement in the gaseous yields, further focus was made on the individual gaseous species yield. The volatiles evolved during biomass devolatilization were attributed to enhanced radical formation

in plastic decomposition with radicals in return acting as H-donors to volatiles evolution.

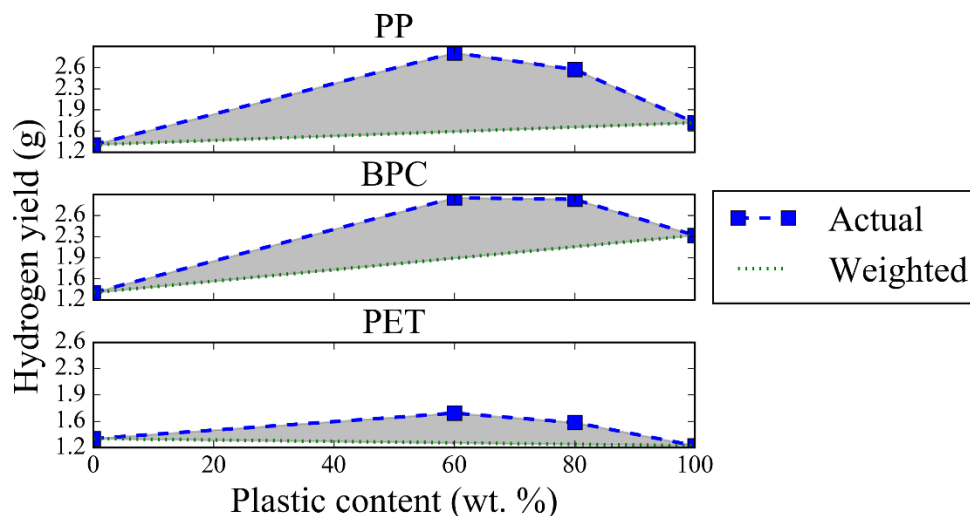


Figure 30. Comparison of cumulative hydrogen gas yields for different plastic/biomass ratios and plastic types.

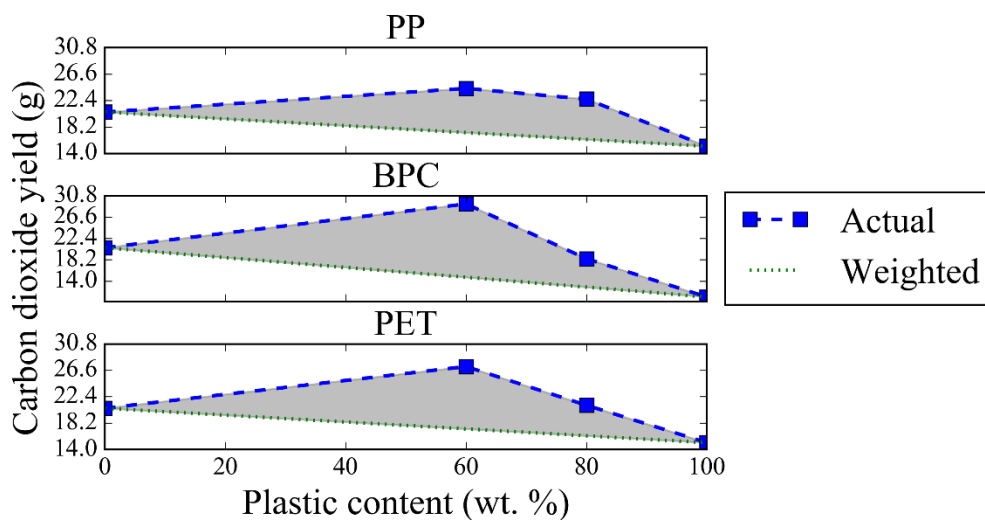


Figure 31. Comparison of cumulative CO₂ gas yields for different plastic/biomass ratios using PP, BPC and PET plastics.

Figure 30 exhibits the hydrogen gas species enhancement using co-gasification of plastics with biomass. The positive enhancement in hydrogen yield supported that the use of biomass with plastics can enhance lighter hydrocarbon formation by

enhanced cracking. Since the gasifying environment was rich in steam, the formed lighter hydrocarbons undergo secondary reactions, such as steam reforming reactions and cracking reactions, to enhance hydrogen and carbon dioxide yields, see Fig. 31. These results along with the previous PE and biomass gasification results [44], revealed almost equally on their mutual involvement in enhanced interaction.

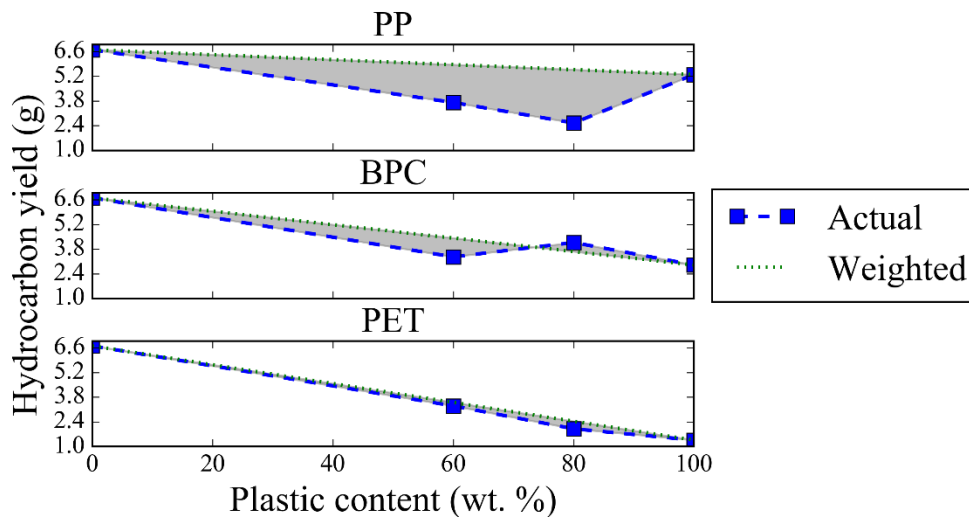


Figure 32. Comparison of cumulative gaseous hydrocarbon yields for different plastic/biomass ratios using PP, BPC, and PET plastics.

Figure 32 reveals the reduction of gaseous hydrocarbon ($\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$) yields by co-gasification compared to mono-gasification when PP was used. Reduction in gaseous hydrocarbons of lesser was of lower significance when BPC was used while PET showed no synergistic effects in hydrocarbon conversion. The synergistic increase in H_2 and CO_2 yields with reduction in gaseous hydrocarbon yields reveals that PP cracking was enhanced during co-gasification along with enhanced reformation of the formed hydrocarbons to yield CO_2 and H_2 . Similar pathway was observed with BPC; the monomers in them also had methyl groups similar to PP which easily reformed to H_2 and CO_2 and lowered gaseous HC yields due to the

presence of biomass. Lack of enough methyl groups in PET monomers along with high content of benzyl bonds and high stability of radicals formed compared to propyl and methyl radicals, was unable to reform leading to only cracking and insignificant steam reforming of the benzyl radicals during the given residence times available in the reactor. The enhanced CO_2 yields observed in Fig. 31 even in PET can be attributed to enhanced decarboxylation in the presence of biomass while primary contributor for CO_2 yields in mono-gasification was from steam reforming and water-gas shift reaction. This can be observed in Fig. 33 which shows the selectivity towards CO_2 during co-gasification compared to mono-gasification. The increase in oxygen content in biomass plastic blends compared to plastic wastes led to increase in the oxidation and increased selectivity towards CO_2 .

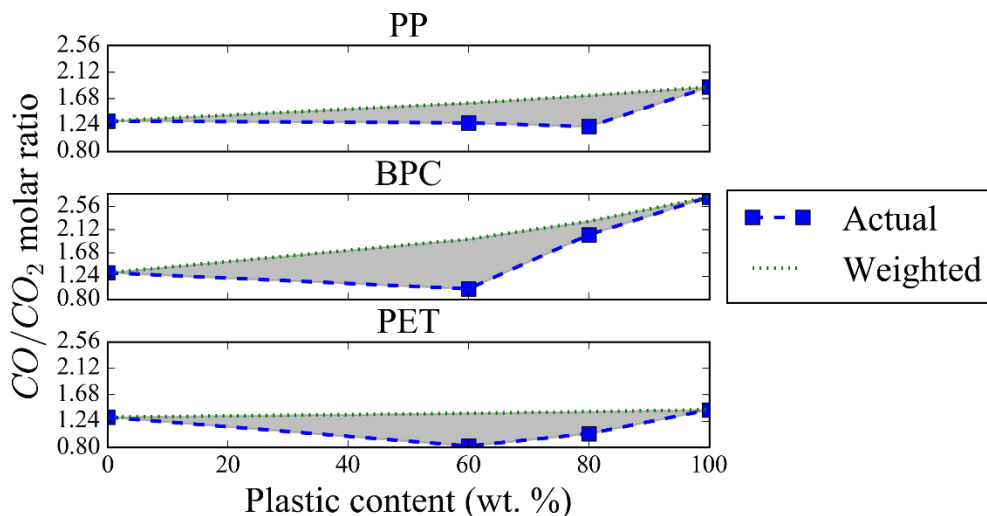


Figure 33. Comparison of CO/CO_2 molar ratio for different plastic/biomass ratios using PP, BPC, and PET plastics.

Figure 34 shows carbon conversion results and correspond to fraction of atomic carbon in the cumulative product gas yield and the solid feedstock. Synergistic effects in carbon conversion can be observed in BPC and PET and not in PP which can be

attributed to enhanced carbon conversion of benzyl radicals in the presence of volatiles from biomass while methyl radicals as in PP had enhanced steam reforming in the presence of biomass. TGA investigations into co-pyrolysis of biomass plastic mixtures to gain insight into the reason for such synergistic behavior. Conversion ($\alpha = \frac{m-m_o}{m_f-m_o}$) was used as the parameter of investigation and it is defined by eq. (1) where m_o is the initial dry sample mass, m_f is the final mass after reaching 1273 K. To understand the synergy, TGA of biomass plastic blends were compared with the combination of the TGA of individual components weighted according to their dry mass content in the initial sample.

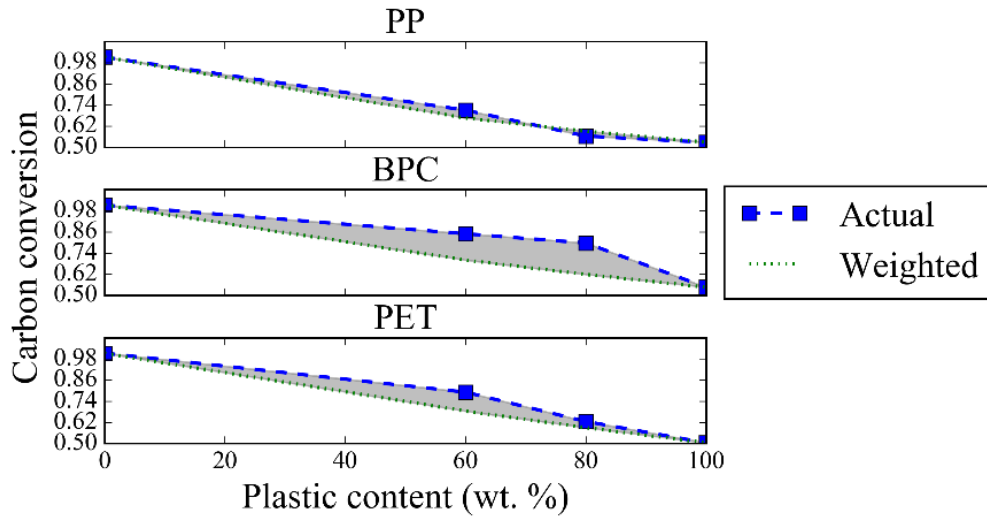


Figure 34. Comparison of carbon conversion for different plastic/biomass ratios using PP, BPC, and PET plastics.

The comparison of weighted conversion rates with experimental conversion rates for different plastic content can be found in Fig. 35-37. Figure 35 showing the comparison for PP reveals no significant divergence of the experimental conversion rate from that of the weighted. Even with increase in the plastic content, its contribution to the solid state reactions was insignificant. This also supports the previous claims that

the volatiles from the biomass and the methyl radicals evolving from PP interact in gas phase reactions and have no contribution to the solid phase reactions on the sample. The presence of synergy in gas yields but its absence from the TGA reveals that the interaction between biomass and PP is confined to gas phase reformation and cracking reactions. It can be predicted that the carbon conversion to gaseous products is not significantly affected by the presence of PP with biomass even though the yield of individual gas components is affected. Fig. 34 also supports such prediction showing no synergistic effects in carbon conversion while individual components can be enhanced from the interactive gas phase reactions as seen by the increase in H₂ yield in Fig. 30.

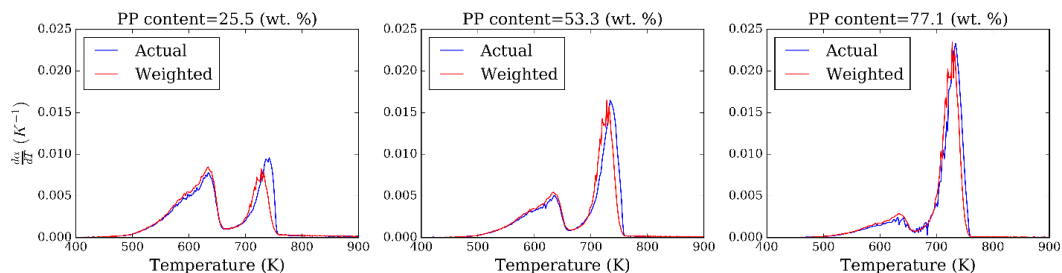


Figure 35. Comparison of co-pyrolysis for different plastic/biomass ratios using PP in TGA

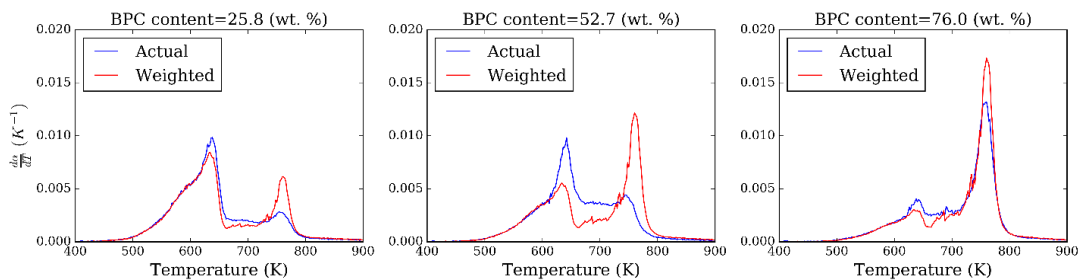


Figure 36. Comparison of co-pyrolysis for different plastic/biomass ratios using BPC in TGA

TGA analysis from co-pyrolysis of BPC and PET with biomass reveal significant mutual interaction between their individual transition peaks. Comparison of

co-pyrolysis with weighted conversion rate in Fig. 36 for BPC reveals a decrease in the peak of pyrolysis expected between 750-800 K and an increase in the biomass pyrolysis peak and the overlapping region around 700 K. This proves the presence of synergistic interaction on the solid phase causing such interacting weight loss. Benzyl radicals as discussed above interact with the biomass volatiles causing such synergy. This solid phase synergy also enhances the carbon conversion as seen in Fig. 34. Similar explanation also can be observed to be the reason for synergy that is also observed using PET with biomass in Fig. 37. Higher benzyl content in BPC compared to PET led to greater synergy using BPC, as observed in co-pyrolysis comparing Fig. 36 and Fig. 37, and in steam gasification as observed in Fig. 34.

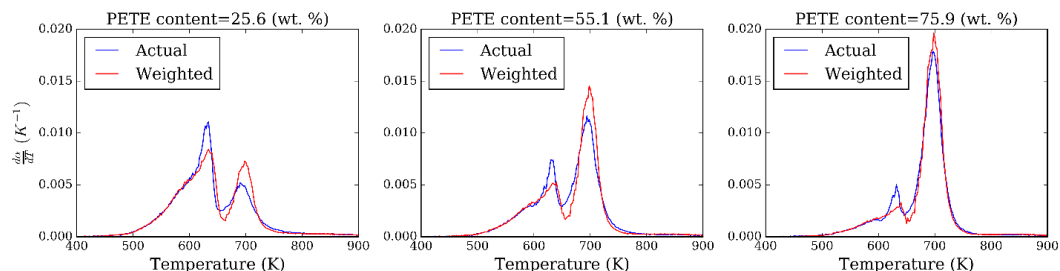


Figure 37. Comparison of co-pyrolysis for different plastic/biomass ratios using PETE in TGA

With enhanced efficiency and carbon conversion using benzyl radicals and increase in hydrogen yields due to methyl radicals and decrease in multiple light hydrocarbon gases suggests improved quality of products (syngas) produced without loss of process efficiency. Examination of such mixtures as feedstocks are encouraged in the pilot/demonstrative phase gasifiers to further support the feasibility issues from the fundamental improved observations given here. Such synergistic enhancement in product gas quality and yields without the loss of efficiency makes co-gasification a

useful strategy for waste to energy production from wastes that are difficult to gasify due to high moisture and ash content or high volatile content.

Chapter 5: Synergistic effects in co-pyrolysis CO₂ co-gasification of paper and polystyrene blends

5.1 Introduction

In this chapter, we will discuss our published investigations carried out on the synergistic effects observed in co-pyrolysis and CO₂-gasification of paper-wastes and polystyrene. Further details can be found in the published article. We will focus on co-pyrolysis and CO₂ co-gasification of different mixtures of polystyrene and office paper wastes to understand the influence of individual feedstocks, their mixture ratios, and the presence of a gasifying agent on the syngas yield and composition. Polystyrene (PS) content in the mixture (% wt.) was also referred to as PC (plastic content) in this chapter.

CO₂ gasification can be an advantageous process in waste to energy, due to the availability of high-temperature CO₂ in multiple industrial flue gases. In addition, utilization of CO₂ is of great interest for atmospheric carbon capture and sequestration development [38,43]. Easier availability of high-temperature CO₂ along with net consumption of carbon emissions for energy makes this process to provide carbon emissions offset [14]. The CO-rich syngas obtained can have wide applications including energy production by syngas combustion and liquid fuel production via biochemical processes such as microbial fermentation (LanzaTech process) for efficient alcohol production [134,135].

These feedstock components were chosen because polystyrene is used in food packaging and other applications are inevitably contaminated by food and paper waste

to make restrict their recyclability and thus ends up in landfills. Polystyrene's high energy density makes it a very useful feedstock for energy production.

5.2 *Results and Discussion*

5.2.1 **Thermogravimetric analysis of paper-polystyrene mixtures**

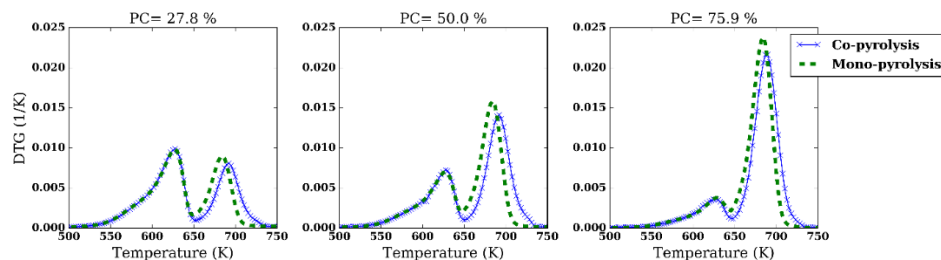


Figure 38. DTG profiles of co-pyrolysis of paper-PS mixtures at heating rate of 10 K/min compared with mono-pyrolysis

The TGA of paper-PS mixtures as shown in Fig. 38 reveals two distinct peaks: one at ~625 K for paper decomposition and the other at ~690 K for polystyrene decomposition. Here mono-pyrolysis refers to weighted results from separate TGA data of paper and polystyrene. Comparison of co-pyrolysis with mono-pyrolysis showed that the presence of paper delayed the polystyrene decomposition and slightly lowered its mass loss rate. This was consistent for different heating rates. Due to the sequential decomposition and lack of overlap, this influence could be from paper char. Similar behavior was observed in the literature when polystyrene was co-pyrolyzed with lignocellulosic wood and charcoal materials.

Table 7. Elemental char surface composition from pyrolysis of paper waste at 1273 K

Element	Paper waste char composition at 1273 K (wt. %)
Carbon	46.24±2.38
Oxygen	29.16±2.73

Calcium	19.98±1.04
Silicon	3.01±0.29
Magnesium	1.6±0.31

Table 7 shows the surface elemental composition of this char. These results show Ca, Si and Mg as the metal species present in paper char that could provide catalytic influence on polystyrene decomposition. Literature shows that the carbonate form of these metals (Ca, and Mg) is known to be catalytic to the char gasification which was apparent via TGA. However, in the current case of paper-polystyrene mixtures with TGA, the delayed polystyrene decomposition and lack of overlap among the paper and polystyrene decomposition peaks suggests that such catalytic enhancement was not present in the solid decomposition reactions [73,136]. While Ca, Si and Mg species may have no positive influence on the chars formed, they could catalytically enhance the secondary reactions on the evolved volatiles from the pyrolysis and gasification of these waste mixtures. Thermal cracking reactions are catalytically active while CO₂ reforming and water-gas reactions are not known to be significantly influenced by Ca, Mg or Si oxides [47,137,138]. Carbon content in char formed from paper/biomass can also be catalytic towards thermal cracking reactions. The catalytic influence of inorganic species on char gasification could still be present in CO₂ gasification, but since polystyrene does not yield char, its influence is limited to gas phase enhancement. While the GC/MS studies showed an increase in alkyl aromatics and decrease in alkenyl aromatics with addition of these materials in the literature, the pathway for such impact remains unknown [108]. The release of alkenyl aromatics does not directly suggest this delay in polystyrene decomposition. A possible

reason for the delay in PS decomposition during co-pyrolysis could be from improved stability of the oligomers formed during PS cleavage in the presence of char.

5.2.2 Product gas and its components' evolution during co-pyrolysis

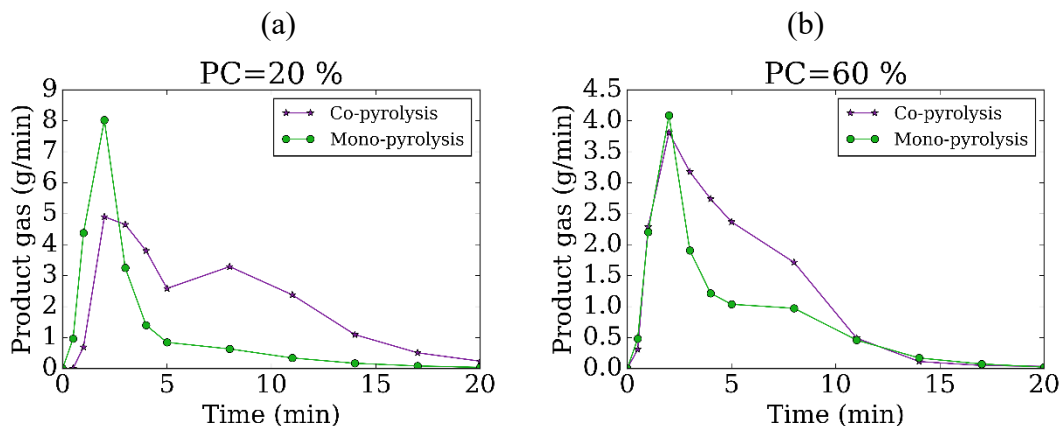


Figure 39. Product gas analysis showing flow rate during co-pyrolysis in (a) and (b) for different polystyrene content

Figure 39 shows the total mass flow rate and yield of the product gas evolved for different initial mass ratios of paper-PS during co-pyrolysis for different PC. The peak at the beginning corresponds to the pyrolytic breakdown of the sample at a high heating rate just after the insertion of the sample into the main reactor held at 1173 K. Pyrolysis completed within 20 minutes. For this chapter, co-gasification/co-pyrolysis refers to experimental product gas flow rate for a specific mixture of paper-PS, while the mono-gasification/mono-pyrolysis refers to the weighted aggregate of the experimental gasification/pyrolysis of the individual components with respect to their initial mass. Figures 39(a, b) reveal that the product gas evolution behavior during co-pyrolysis varied from the expected aggregate of individual component pyrolysis. While the peak flow rate was lower than expected, the evolution continued for longer duration producing higher flow rate after 5 minutes for both the feedstock ratios. This delayed

evolution was captured in the TGA results shown in Fig. 38, which showed delayed PS decomposition. At the high heating rate, as in semi-batch reactor, this effect was more pronounced, but it leads to synergistic enhancement in gaseous yield for low polystyrene content. To understand this synergy further, we will discuss the evolution of individual syngas components and energy.

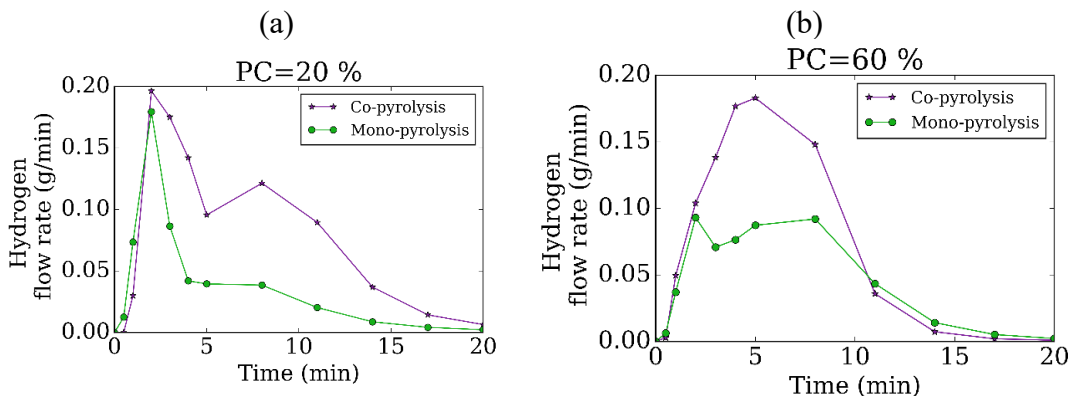


Figure 40. Hydrogen flow rate during co-pyrolysis for different polystyrene content

Figures 40(a,b) shows the evolved H_2 flow rate and yield during co-pyrolysis different feedstock ratios and compared with the weighted aggregates of the individual component pyrolysis at the same operating conditions. It reveals a significant deviation of H_2 yield from co-pyrolysis compared to mono-pyrolysis. While the peak evolution time was almost the same as expected from individual component pyrolysis, the net flow rate was almost double than that of the expected yield. The volatiles from paper pyrolysis could be responsible for increasing the rate of polystyrene decomposition, yielding higher H_2 from thermal cracking. This enhancement in H_2 could be from mutual kinetic interaction or directly from the difference in CHO composition of the sample with varying PCs. Increase in PC increased the H_2 yield but its evolution is highest from 5-10 minutes as opposed to 2-5 minutes for low PCs.

(a)

(b)

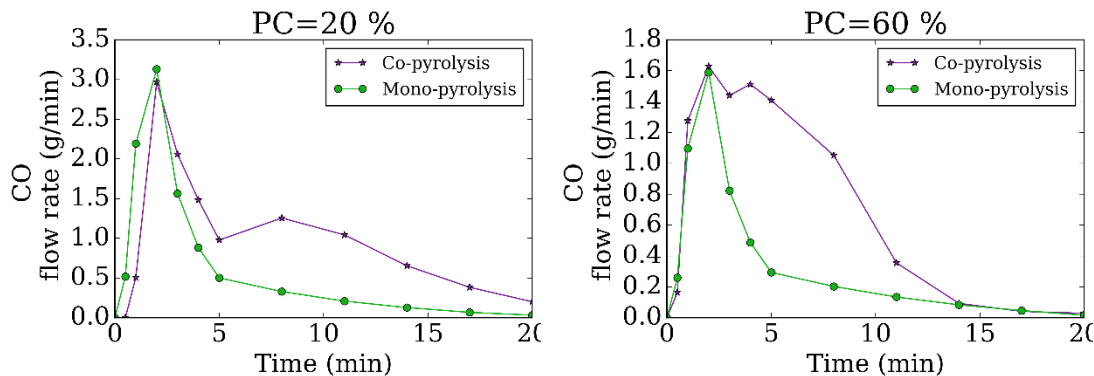


Figure 41. CO flow rate during co-pyrolysis for different polystyrene content

Figures 41(a, b) show the evolution and yield of CO during co-pyrolysis for different mixture ratios. During the first 10-15 minutes, pyrolytic breakdown and secondary reactions cause CO formation as seen in co-pyrolysis. CO evolution seems like a combination of two peaks, one within 5 minutes and the other after this time. Since there is no O content in polystyrene, there should be no CO from it except for some reaction with the evolved gases from paper pyrolysis. CO contribution from polystyrene is significant during co-pyrolysis and this cannot be predicted using mono-pyrolysis curve which ignores mutual interaction. This could be from the oxygenated volatiles from paper pyrolysis interacting with the free radicals from polystyrene. Since the time duration of this evolution is small, it suggests that this interaction for CO enhancement is in gas phase because solid-gas interactions are slow compared to gas-phase reactions. While CO enhancement is from secondary reaction interaction, enhancement in decomposition in co-pyrolysis could still be present. Increase in H_2 yield along with an increase in gaseous hydrocarbon yield suggests that the interaction is not only gas-phase as depicted by CO, but also in enhancing solid mass loss to form volatiles during this initial phase of 10 minutes.

5.2.3 Comparing cumulative yields during co-pyrolysis and CO_2 co-gasification

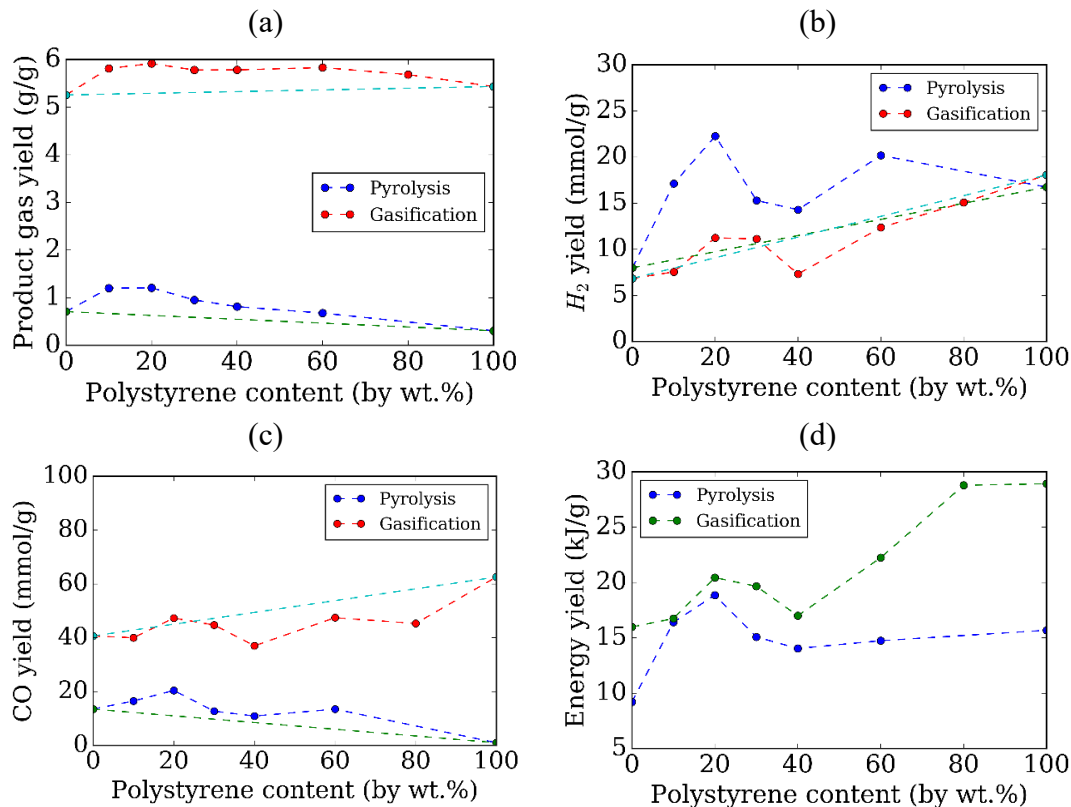


Figure 42. Cumulative yields of (a) product gas, (b) H₂, (c) CO, and (d) total energy yield from co-pyrolysis and co-gasification (with respect to initial feedstock mass) for different feedstock ratios

The cumulative yields were obtained for the syngas components, and the total syngas energy from co-pyrolysis and co-gasification. A synergistic enhancement of the product gas yield can be noticed in the co-pyrolysis curve showing the highest deviation from weighted results for PC~10-30% in Fig. 42(a). The net product gas evolved reduced with an increase in PS content, possibly due to increased production of aromatics with better thermal stability leading to lower thermal cracking and thus lower gas yields. Even in co-gasification, increase in PC decreased product gas yield, also possibly due to aromatic evolution which is less active towards CO₂ reforming. Addition of 10-20% PS not only resulted in highest product gas yield but also

significant synergistic effect. This means, while the mixtures of paper-PS can mutually interact for varying compositions, significant paper content is needed to enhance the PS decomposition. From the TGA understanding, high paper content means high char/solid intermediate yields which, although can delay depolymerization, can act as a catalyst in cracking of the oligomer free radicals evolved from PS decomposition leading to enhanced gas yields. Further understanding into this synergistic influence needs dwelling into the individual gas component yields and flow rates.

From Fig. 42(b), co-gasification produced almost same H_2 as individual component gasification, but as the PC increased, co-gasification produced lower H_2 than mono-gasification although net H_2 increased with increase in PC due to high H/C in polystyrene. Increase in PC also delayed H_2 evolution, possibly due to higher stability in aromatics obtained from PS causing lower H_2 yield [121]. CO_2 gasification decreased H_2 yield compared to pyrolysis, due to reverse water gas shift reaction, leading to H_2O formation along with CO formation at such high temperatures.

From Fig. 42(c), one can see CO flow rate during CO_2 co-gasification to be lower than expected from individual component gasification. For low PC, CO evolution during the initial 5 minutes was higher for co-gasification, accounted by the enhanced co-pyrolysis mentioned earlier. After this time, the CO evolution from char gasification is almost the same as predicted from mono-gasification. But at high PC in co-gasification, while the CO evolution was almost the same as mono-gasification during the pyrolytic breakdown, CO evolved from char gasification (5-50 min. duration) was much lower during co-gasification compared to mono-gasification. The reason for this could be from enhanced PS decomposition in the paper-PS mixture. The results show

that the decomposition rate is enhanced in co-pyrolysis. This means higher volatile yield, which results in lower char remaining. So, as the char (left after $t=10$ minutes) decreases by mutual interaction, char left for Boudouard reaction is low resulting in lower CO. Comparing different PCs for CO evolution in char gasification, one can also see that for low PC, co-gasification yielded similar CO compared to mono-gasification. But at high PC, CO from char gasification was lower compared to mono-gasification. CO was the main contributor to syngas. So, co-gasification globally decreases the syngas yield compared to the individual gasification. However, it produces more syngas than pyrolysis and utilizes the CO_2 . Both processes solve the feeding issue of polystyrene. At low PC, most of the char residue in Boudouard reaction, is from paper, while the char residue at high PC corresponds to PS. Fast devolatilization of paper before PS influenced PS decomposition while the PS is still in stable melt-phase during paper decomposition. The lowering of CO due to low char forming tendency is supported by CO_2 evolution behavior showing lower CO_2 consumption during co-gasification and thus leading to increased CO_2 presence in the product gas.

The results presented have shown that co-pyrolysis of paper with polystyrene increased the gas yield while the char yields reduced to result in lowered CO yields during CO_2 gasification. Sufficient residence time/ downstream processing of the volatiles formed from co-gasification of paper-PS can enhance the syngas yield. To cumulatively understand the influence of using paper-PS mixtures as opposed to pure components in pyrolysis and gasification, we examine the heating value of the product gas. Energy yield here refers to the sum of the mass yield of each component in the syngas multiplied by their respective lower heating value (LHV). Thus, the obtained

yield is divided by the initial mass of the sample (35 g). This provided us the energy that could be extracted from the syngas assuming very high combustion efficiency, which is the case in gas phase combustion unlike combustion of solid fuels such as coal.

From Fig. 42(d), a comparison of co-pyrolysis with mono-pyrolysis reveals significant enhancement in the energy yield due to an increase in the gaseous hydrocarbon evolution along with H_2 due to a synergistic interaction between paper-PS. The synergistic enhancement was highest for low PCs which coincides with the H_2 yield behavior. The total energy yield increases with PC theoretically but, due to the synergistic influence, the highest energy yield corresponds to PC=20%. In co-gasification, the enhancement in energy yield by co-pyrolysis is negated by the reduction in CO yield during co-gasification leading co-gasification having no significant influence on energy yield compared to mono-gasification.

Chapter 6: Kinetics of synergistic effects in the co-pyrolysis of biomass with different plastic wastes

6.1 Introduction

Understanding the kinetic and mechanistic aspect of the pyrolysis and gasification is essential to improve their process design and viability. In the literature, kinetics of biomass decomposition was examined using thermogravimetric analysis (TGA) and pathways using micro-pyrolyzer. The decomposition products were analyzed using mass spectroscopy (TGA-MS), Fourier-transform infrared spectroscopy (FTIR), gas-chromatography (TGA-GC or TGA-GC/MS) [139–141]. Syngas or liquid yields obtained using fixed bed, and fluidized bed or lab scale semi batch reactors provided quantify the product syngas yield for different feedstocks and operational conditions [33,142,143].

In-situ FTIR studies of lignocellulosic wastes revealed that at initial temperatures between 473-673 K, the peaks of O-H, C-OH, C-H, and C=O increased, but as the temperature increased, C=O and C-H decreased to form CO and CO₂, while C-C decreased to form CH₄ and C-H decomposed to form H₂ [141]. In the case of plastic wastes, the composition of product yield depends significantly on the monomeric structure of these plastics – straight chains yielded H₂ and hydrocarbons [144], while aromatic and C-O-C linked polymers yielded CO, CO₂ and char so that aromatics were involved in decarboxylation, dehydration along with rearrangement reactions. Molecular pathway modeled for decomposition of different types of plastics is given [145].

Interest in co-pyrolysis and co-gasification of different types of biomass and plastic wastes has increased due to common availability of these feedstocks in wastes. Co-pyrolysis of cellulose and polypropylene showed activation energy reduction and revealed lowered char yield from co-pyrolysis compared to individual pyrolysis. This was attributed to H-abstraction in polypropylene leading to radical formation from cellulose and OH from cellulose reacting with polypropylene oligomer radicals to form long chain alcohols along with biomass char catalyzed propylene pyrolysis [146–148]. Enhanced syngas and hydrogen yields from steam gasification and bio-oil yields from fast pyrolysis of biomass-plastic blends were demonstrated in fluidized bed and fixed bed reactors [83,96,119,133,149–153]. Investigations into the influence of synergistic effects of co-pyrolysis on the pathway, the kinetics of conversion and products evolution along with intermediates speciation are essential to further our knowledge on understanding the exclusive pyrolysis of biomass (lignocellulose) and plastic materials.

TGA conversion of lignocellulosic materials was modeled by different types of models, of which, distributed activation energy model (DAEM) stands out due to its ability to consider the effect of varying activation energy distribution, depending on the types of bonds present in the feedstock [141,154,155]. While DAEM is a parallel reactions model, other models which consider an aggregate of sequential and parallel degradation pathways such as Broido-Schafizadeh scheme, were also investigated in the literature [156]. A comparison of different reaction pathway models and fitting using genetic optimization algorithm, using cellulose was discussed in ref. [156]. A derivation of DAEM (formulation given in Chapter 2) is used to represent the contribution of individual components in both naturally mixed materials of only

lignocellulose materials and artificial blends of biomass-plastic mixtures. This will help provide quantitative differences in gasification of individual components compared to biomass-plastic blends [126]. This has motivated us to use DAEM for all mixtures but with a higher number of pseudo-components.

This chapter examines kinetics of co-pyrolysis of biomass and plastic wastes using different types of plastics. Pinewood was chosen here as the lignocellulosic biomass material. Recycled polymer pellets of black polycarbonate (BPC), polyethylene terephthalate (PETE), and polypropylene (PP) were chosen for the plastics since they vary in their monomeric O/C content, energy content, and the linking bonds. While BPC and PETE contain aromatic content, they vary in the polymer linkage, but PP is significantly different from these two as it has no aromatic content, and the polymeric linkage is between C-C bonds. Investigations were carried out using TGA to understand the influence of heating rates, composition of plastics in the mixture on the activation energy, reaction rates and contributions of individual components using DAEM as described in Chapter 2. This will also help increase comprehension of synergistic effects observed and reported in Chapter 4.

6.2 Results and Discussion

6.2.1 Individual pyrolysis of biomass and plastics

TGA evaluation of the three different plastic polymers used were first conducted in solo (individually without any blends with the biomass). In this section, we focus on gaining insight into pyrolysis of different types of polymers, their transition peaks and rate of decomposition.

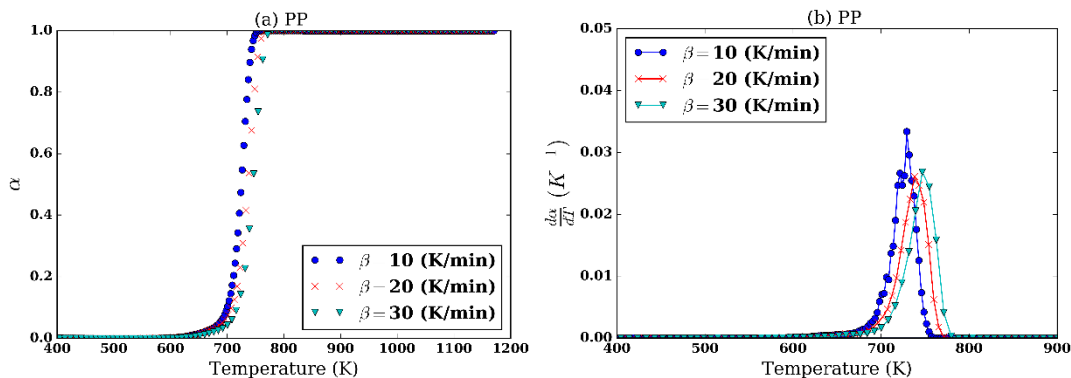


Figure 43. Progress of (Left) conversion (α), and (Right) the rate of conversion (da/dT) in polypropylene pyrolysis at different heating rates (β)

The pyrolysis of polypropylene decomposition is reported first. Figure 43(a) shows non-isothermal conversion of PP pyrolysis with temperature while Fig. 43(b) reveals the rate of conversion with temperature at different heating rates. From these figures, one can see that the contribution of PP to pyrolysis reaction starts at around 700 K and peaks at 730 K for $\beta = 10 \text{ K} \cdot \text{min}^{-1}$. The peak in Fig. 43(b) is apparent to be symmetric, which signifies that PP pyrolysis can be constructed by a narrow range of reactions. This is expected because of PP's relatively simple monomeric structure, which means a less variety in the type of bonds present. Almost all the synthetic polymers were proposed to decompose via radical mechanism. C-H bonds of primary, secondary, and tertiary C atoms, and C-C σ are the only bonds present that makes probability distribution in bond selection for radical formation or breakage. Since the char formed from polypropylene pyrolysis is very low ($\sim 2\%$ of the dry initial weight), this means that its radical mechanism is very rapid, and the formation of lower hydrocarbons is favored by more breaking of C-C bonds than the breaking of C-H bond. The invariance in the shape and height of the peaks in the rate of pyrolysis with respect to heating rate also supports the absence of structural and shape effects of the sample chosen. The

peaks, although were invariant in shape and height maintained at $.026 \text{ K}^{-1}$, shifted by a well-known phenomenon of temperature lag that is caused by material decomposition in the TGA at high heating rates. The peak temperature moved from $T=730 \text{ K}$ to 746 K as the heating rate (β) moved from 10 K.min^{-1} to 30 K.min^{-1} . These results were used further to investigate the effect of lignocellulosic content on polypropylene pyrolysis.

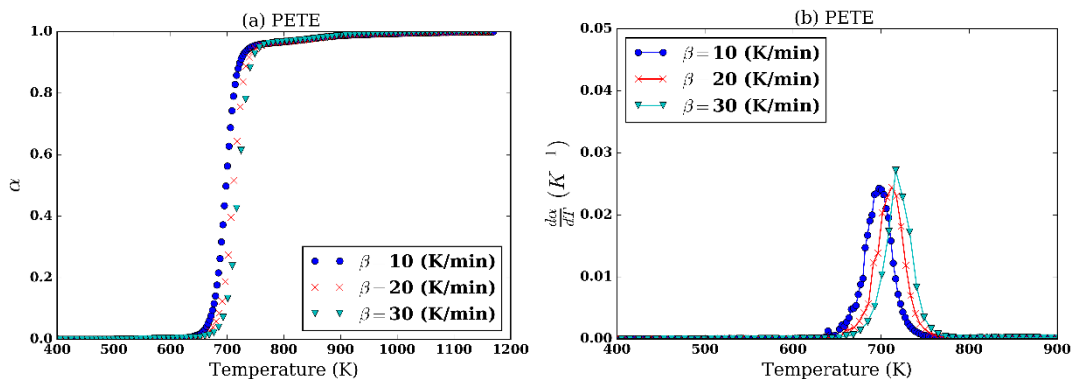


Figure 44. Progress of (Left) conversion (α), and (Right) the rate of conversion (da/dT) in polyethylene terephthalate pyrolysis at different heating rates (β)

Pyrolysis of PETE under similar conditions was also conducted to obtain the pyrolytic characteristics of pure synthetic polymers before mixing with any lignocellulosic material. Figure 44(a, b) show the evolution of PETE pyrolysis conversion and its rate with temperature at different heating rates. The temperature of peak height varied from 697 K to 716 K with increase in β from 10 K.min^{-1} to 30 K.min^{-1} . The peak height was maintained at $.024 \text{ K}^{-1}$ with no significant effects of increase in heating rate. Although the start of conversion in Fig. 44(a) was sharp from around 650 K, the end had a gradual path to reach complete conversion that ranged from 710 K to 850 K. This asymmetry can be explained from a much wider variety of bonds present for radical formation unlike PP. Literature reveals that as the conversion of PETE progresses, the net aromaticity of the sample increases from the loss of less strong aliphatic bonds [157]. The breaking of ester functional groups attached to benzyl

portion will lead to the decomposition of polymer core and release of CO₂ via decarboxylation. In parallel with ester rearrangements, the broken linkages form carbonyl groups, which decomposes to release CO. This is followed in parallel by cyclization and aromatization via H abstraction leading to char formation, which occurs in parallel with breaking of the aromatic structure to release H₂ and lower molecular weight hydrocarbons. The char formed by the end of PETE pyrolysis is high, around 15% of the dry initial weight, compared to PP. Cyclization followed by dehydrogenation is favored due to the presence of benzyl intermediates, which due to their relatively higher stability, increases the favorability of this pathway causing eventually larger amounts of char formed.

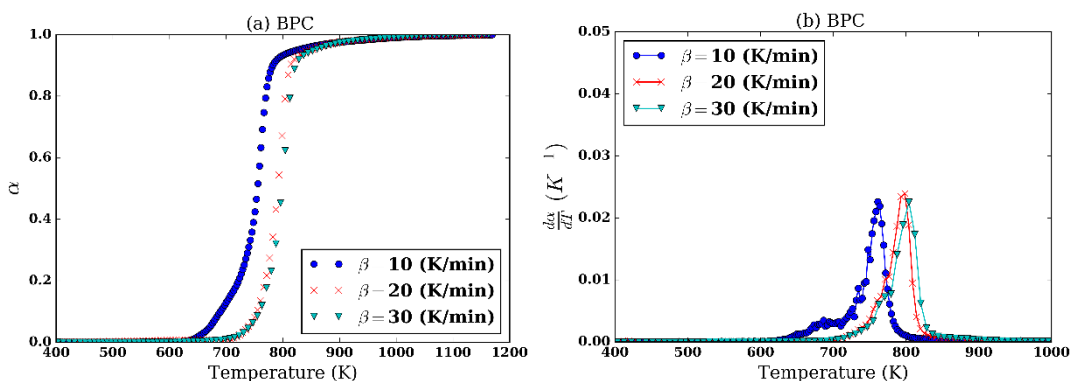


Figure 45. Progress of (Left) conversion (α), and (Right) the rate of conversion (da/dT) in polycarbonate pyrolysis at different heating rates (β)

The evolution of BPC pyrolysis characteristics from the TGA experiments, for the conditions as given above, are presented in Fig. 45(a, b). The peak of BPC pyrolysis varied from 761 K to 804 K by varying β from 10 K.min⁻¹ to 30 K.min⁻¹ while the height stayed at .022 K⁻¹. Unlike PP and PETE pyrolysis characteristics, the start of BPC decomposition was gradual, as shown in Fig. 45(a), while the end of BPC pyrolysis, similar to PETE pyrolysis, was gradual. The presence of benzyl groups in BPC backbone structure makes the latter part of BPC pyrolysis similar to PETE

pyrolysis causing benzyl radical driven stability and its associated pathway for charring along with a later peak of pyrolysis as compared to PP and PETE. From Fig. 45(b), we can also see that the initial portion of BPC pyrolysis starts slowly reaching a local plateau in $d\alpha/dT$ for $\beta=10 \text{ K.min}^{-1}$ at around 700 K. This means initially the ester portions of the chains break to form oligomers followed by the decarboxylation and dehydration to release CO and CO₂ starting from its earlier phase [59]. This continues gradually, owing to rearrangements and decarbonylation along with carboxylation. This leads to the formation alcohols and phenols from the loss of CO as seen by evolved gas analysis [59], followed by the parallel pathways of aromatics breaking to form hydrocarbons and H₂ along with char formation from cyclization and aromatization.

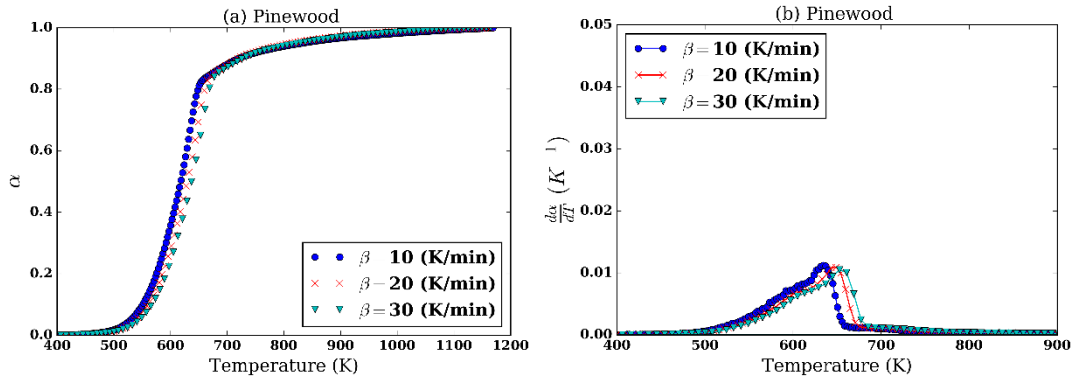


Figure 46. Progress of (Left) conversion (α), and (Right) the rate of conversion ($d\alpha/dT$) in pinewood pyrolysis at different heating rates (β)

Exclusive pyrolysis of pinewood for different heating rates is shown in Fig. 46(a, b). The complex aggregate of hemicellulose, cellulose and lignin present in pinewood makes the pyrolysis more distributed starting at 500 K and continuing until 670 K. The decomposition peak shifts from 634 K to 650 K with increase in heating rate from 10 K.min⁻¹ to 30 K.min⁻¹. Initial decomposition starts with dehydration, followed by decarboxylation and decarbonylation. This evolves H₂O, CO, and CO₂ starting the pyrolysis of pinewood. Decomposition of anhydride saccharides is a complex process

evolving methane and other hydrocarbons. Apparent lignin decomposition starts later than cellulose and hemicellulose contributions and continues until the end of pinewood pyrolysis. Lignin consisting of phenyl ether bonds break to release phenols and benzyl compounds with carboxylic acid functional groups. These phenols can cause heavy molecular weight molecules to form due to stability of the phenolic intermediates. Detailed pathways of lignocellulosic materials is not the focus here and can be found in detailed reviews [141,158].

6.2.2 Co-pyrolysis of biomass and plastics

Co-pyrolysis of biomass (pinewood) with different kinds of plastics and different compositions of the blends were used to understand the mutual synergistic interaction and its effect on the pyrolytic behavior of the ensemble sample. Different types of plastics were mixed with pinewood in different mass ratios. The plastic content in these blends were 25%, 50% or 75% with respect to the total dry mass of the sample. Since all the synthetic polymers chosen in this study were thermoplastic, they melt without change in the composition before significant decomposition characteristics occurs. This makes these pyrolysis results invariant with respect to the method of mixing biomass with each of the plastics as the melted polymer will evenly mix with the biomass sample. The DTG ($d\alpha/dT$) of co-pyrolysis results were compared with the weighted addition of DTG of the individual components when pyrolyzed separately. The weights for this will be their respective initial mass content in the initial dry sample. This comparison will reveal the presence of mutual interaction on a heterogeneous scale involving the solid sample in the holder with its components and the evolved

volatiles so that the results will signify the importance of co-pyrolysis as compared to individual component pyrolysis.

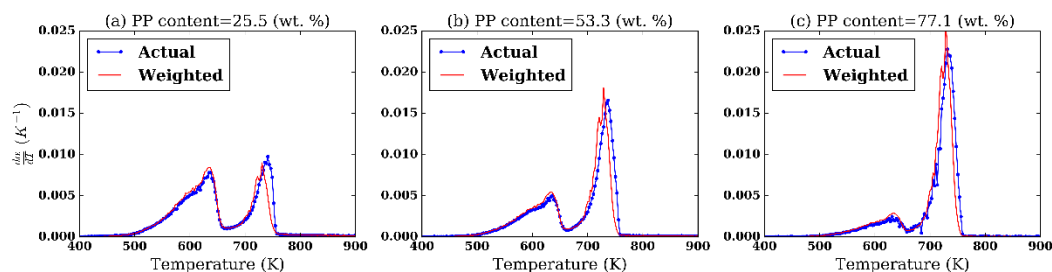


Figure 47. DTG of co-pyrolysis of PP with pinewood for plastic content of (by dry initial wt.) (Left) 25.5%, (Middle) 53.3%, and (Right) 77.1%

Co-pyrolysis DTG of PP with pinewood along with the DTG computed from the weighted aggregate of DTGs of individual component pyrolysis is presented in Fig. 47(a-c). PP pyrolysis with biomass reveals that such mutual interaction was not significant from these experiments. The enhancement of co-pyrolysis of PP with wood derived materials was mainly attributed to char formed from the wood mixed [118]. As the char formed from the wood based materials was before the start of PP pyrolysis, it acted as a catalyst in the enhancement of PP cracking [147]. Under certain ratios, addition of wood based materials to PP was found to increase the stability of the composite due to diffusional limitations [148]. This reveals that the presence of aliphatic hydrocarbon based synthetic polymers, although can enhance the product quality when co-pyrolyzed with biomass due to their role as H-donor, it cannot necessarily be observed with all kinds of lignocellulosic materials. Comparison between charcoal-PP and wood-PP blends, similar to the observations here, showed significant enhancement in PP pyrolysis in the presence of charcoal but since formation of char from the wood was delayed and overlapped insignificantly on the PP pyrolysis peak, such effect was not profound with the wood-PP composites [147]. So, synergistic

effects from the addition of PP to lignocellulosic content were mainly catalytic and the interactive effects cannot be observed from DTG comparisons.

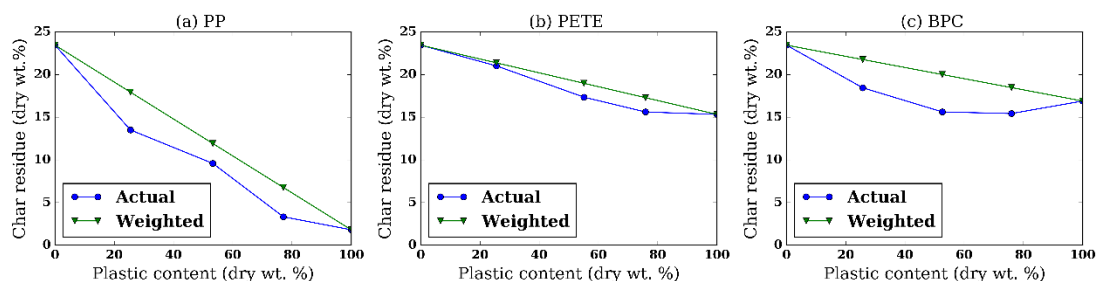


Figure 48. Comparison of char residue from the co-pyrolysis of pinewood and (Left) PP, (Middle) PETE, (Right) BPC with weighted aggregate residue of individual component pyrolysis

Figure 48(a) shows a comparison of char residue formed from co-pyrolysis of PP with pinewood as well as weighted aggregate of the char residue formed from the pyrolysis of individual components. The weights of this aggregate were chosen to be their respective initial mass content in the dry composite sample. The results reveal that even though the comparison of the rates of pyrolysis showed no synergistic effects, the net carbon conversion to gases/vapors or the formation of char residue was significantly affected compared to individual component pyrolysis. PP pyrolysis provided relatively low char residue compared to biomass pyrolysis. But when combined, this PP addition enhanced the biomass pyrolysis causing an increase in the net carbon conversion of the biomass to volatiles and gases, thus lowering the net char residue. The explanation showing increased stability of PP/wood composites as discussed above supports the rationale here. The PP melt that forms at biomass pyrolysis temperature range, before PP pyrolysis peak, provided an ideal H-donor rich phase/platform for the decomposition of biomass. This was not observed in DTG because the interaction between biomass and PP did not increase the net evolution rate of volatiles from biomass. Instead, it provided a platform which enhanced volatiles formation, but they

did not escape the PP melt and instead stayed in the sample holder and reacted with the PP to help decompose. The radicals stabilizing them with the oxygenates from the biomass formed long chain alcohols when PP acted as H-donor to enhance hydrogenation of biomass volatiles [148].

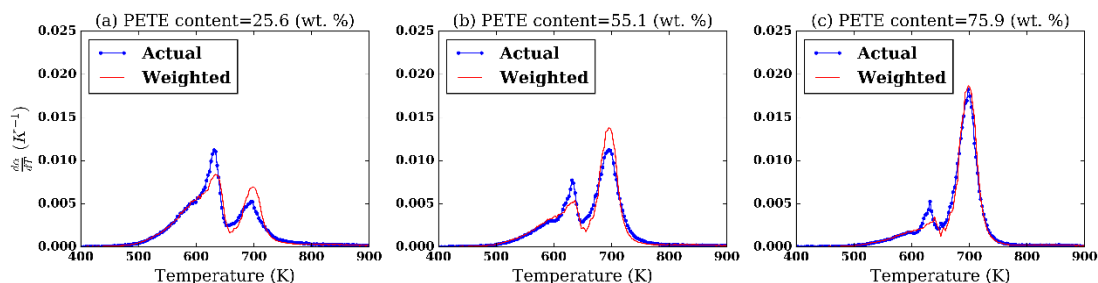


Figure 49. DTG of co-pyrolysis of PETE with pinewood for plastic content of (by dry initial wt.) (Left) 25.6%, (Middle) 55.1%, and (Right) 75.9%

The DTG of co-pyrolysis of PETE synthetic polymer with biomass, for different plastic content conditions, is presented in Fig. 49(a-c), along with the DTGs of individual component. Influence of synergistic effects was apparent using PETE and it can easily be seen in Fig. 49(a, b), unlike PP. Addition of PETE to biomass increased the rate of volatile evolution during biomass decomposition and lowered the peak corresponding to PETE pyrolysis compared to the weighted DTG. Lignin contribution from the biomass spread over wide range of temperatures and its phenolic ether content can interact with the benzyl ester intermediates formed from PETE polymer de-linkage. These intermediates can react to form more stable intermediates, thus improving the energetics and enhance the probability of proceeding in such a pathway. Also, the carboxylic acid and ester intermediates from PETE can also stabilize by interacting with the carbonyl groups which tend to form from cellulose and hemicellulose dehydration. It is conjectured that the pyrolysis of PETE occurs via anhydride formation. Such an anhydride can easily form in the presence of biomass leading to

increased overlap region and lowered peak region. Detailed pathway design for such synergy needs further investigations to further enhance our knowledge on the reasons or pathways for enhanced biomass decomposition. Residues from co-pyrolysis of PETE with pinewood shown in Fig. 48(b) also reveal the presence of synergistic effects, which enhance the net carbon conversion and lower the char formation compared to the char yield from individual component pyrolysis.

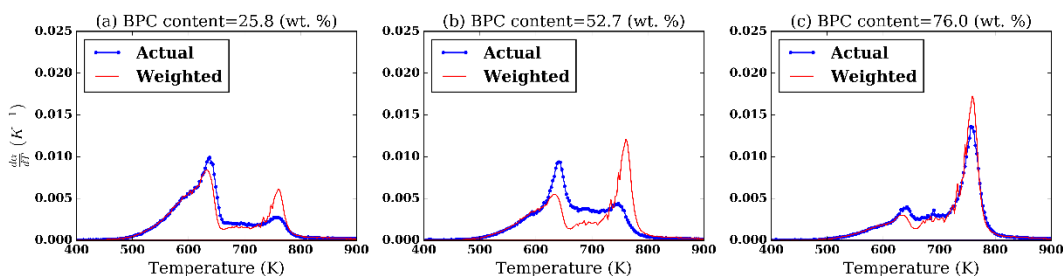


Figure 50. DTG of co-pyrolysis of BPC with pinewood for plastic content of (by dry initial wt.) (Left) 25.8%, (Middle) 52.7%, and (Right) 76%

Co-pyrolysis of BPC and pinewood was conducted, similar to the other polymers. The obtained DTGs results shown in Fig. 50(a-c) are for different plastic contents. Synergistic effects appear to provide similar effect as for PETE but more significantly using BPC in terms of decreasing the plastic polymer peak and increasing the biomass decomposition peak. BPC flows above 420 K and mixes evenly with the biomass before start of the biomass decomposition. Such a fluidic phase enhances biomass decomposition especially the cellulose and lignin contributions. BPC decomposition tends to produce more phenols via removal of CO and CO₂. Favorability of such a pathway can be enhanced in the presence of biomass by forming stable phenolic intermediates with the lignin portion that also mutually enhances biomass conversion and breakdown to form low molecular weight aromatics which can form as volatiles thus aiding in avoiding or decreasing char formation. This is apparent from

Fig. 48(c) that shows lowered char formation via co-pyrolysis with most synergy corresponding to plastic content of 55.1% by wt. causing reduction in char by some 10 %. Cellulose dehydration can also be enhanced in the presence of BPC via radical stabilization which favors functional groups leaving easier to form low molecular weight aromatics, hydrocarbons, and stable gases, such as CO, H₂O, and CO₂.

6.2.3 DAEM in co-pyrolysis of biomass and plastics

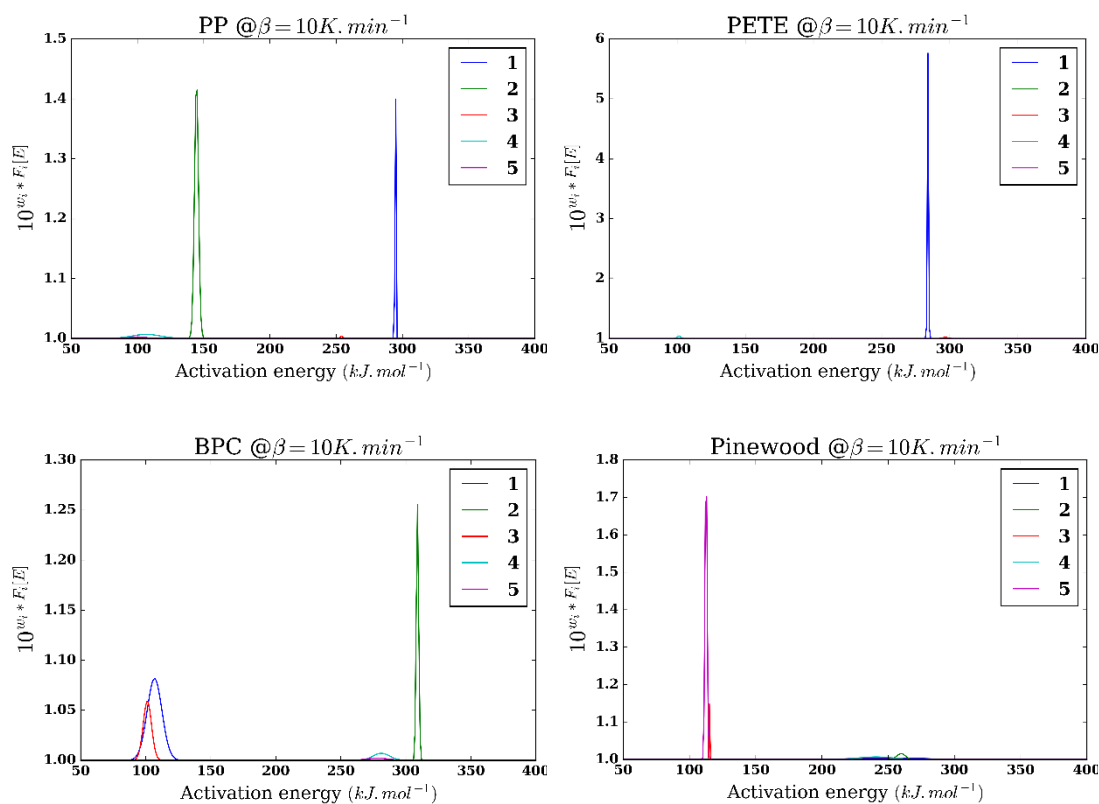


Figure 51. Weighted activation energy distribution from DAEM of individual component pyrolysis at 10 K. min⁻¹ (y axis in 10^x scale, and the legend represents the pseudo component). Top left: PP, Top right: PETE, Bottom left: BPC, and Bottom right: Pinewood.

Distributed activation energy model (DAEM) was used for fitting the DTGs of pyrolysis of biomass and plastics and compared with the fitting parameters when fitted

to co-pyrolysis of biomass with different plastics. This modeling analysis can be represented as the transformation of the DTGs (da/dT vs. T) into an activation energy plane where the pyrolysis is represented by the distribution of activation energies of reactions required to recreate such a DTG evolution. Such analysis provides valuable insight into the pyrolysis kinetics of different materials revealing the number of lumped sets of reactions that are involved by the number of pseudo-component contributions required, as well as the activation energies of these reactions. The number of pseudo component contribution also points to the direction of providing insight into possible variation in the reaction mechanism by co-pyrolysis or the presence of additional sets of intermediates changing the reaction pathway. Such analysis can be done by comparison of the product of the weighted coefficient (w_i) and the activation energy distribution ($F_i(E)$) of that component. All the conditions were modeled with a 5 pseudo-components DAEM model formulated for 1st order reactions as given in Chapter 2.

Table 8. The model parameters of fitting 5 component DAEM to different test conditions

Condition s/ parameter s	PP	PETE	BPC	Pinewood	PP + pinewood (PC=53.5 %)	PETE + pinewood (PC=55.1 %)	BPC + pinewood (PC=52.7 %)
w_1	0.27847 9	0.88651 8	0.49484 7	0.11538 3	0.686518	0.495137	0.31513
$\log_{10}(k_1)$	19.6217 8	19.7855 3	19.7479 8	19.1302 8	19.71414	19.80857	19.5538
$E_{0,1}(\text{kJ/mol})$	294.618 6	283.984 6	106.770 7	249.678 3	115.2244	104.1409	256.8524
$\sigma_{0,1}(\text{kJ/mol})$	0.26016 8	0.46476 6	5.78994	31.8154 9	9.19728	11.03705	0.728195
w_2	0.62072 6	0.00108 9	0.23473 3	0.05509 4	0.041583	0.174444	0.069354
$\log_{10}(k_2)$	19.7596 8	19.9867 1	19.7991 4	19.7068 5	19.62004	19.36958	19.46091
$E_{0,2}(\text{kJ/mol})$	144.553 4	225.749	308.939 1	259.761 4	230.2309	282.0462	295.1342

$\sigma_{0,2}(\text{kJ/mol})$	1.57906 4	14.9250 4	0.94478 7	3.30982 9	13.09986	2.069264	10.59886
w_3	0.00459 5	0.04231 1	0.20225 8	0.17400 4	0.060238	0.149033	0.402197
$\log_{10}(k_3)$	19.0255 1	19.8767 1	19.6123 8	19.8736 6	19.61032	19.48113	19.99216
$E_{0,3}(\text{kJ/mol})$	254.062 4	296.718 8	101.225 9	114.755 7	253.3057	102.4293	105.1171
$\sigma_{0,3}(\text{kJ/mol})$	1.07954 9	1.97427 3	3.23945	0.11352 2	8.532685	16.42085	1.334832
w_4	0.07959	0.05497 5	0.04889 9	0.09870 7	0.135762	0.045478	0.155127
$\log_{10}(k_4)$	18.4194 1	18.8941	19.6278 3	19.5084 6	19.73246	19.85004	18.86997
$E_{0,4}(\text{kJ/mol})$	106.710 9	101.407 1	281.106 5	240.797 5	132.4266	253.3976	259.7742
$\sigma_{0,4}(\text{kJ/mol})$	10.8566 2	1.25848 7	6.48519	13.2003 7	7.95762	1.229381	28.1447
w_5	0.01661	0.01510 7	0.01926 3	0.55681 2	0.075898	0.135907	0.058192
$\log_{10}(k_5)$	19.8336 8	19.7650 9	19.9998 9	19.6784 2	19.43628	19.8137	19.63283
$E_{0,5}(\text{kJ/mol})$	100.427 3	347.920 7	278.121 6	112.519 1	295.1534	262.7415	264.88
$\sigma_{0,5}(\text{kJ/mol})$	6.03755 5	22.2684 7	8.04586 5	0.80494 5	0.644517	30.9098	30.8388
Obj (%)	2.9	2.5	3.01	2.1	2.18	3.28	3.48

Initially, the DAEM was fit to the DTGs of individual component pyrolysis of pinewood, PP, PETE, BPC. Then, the DAEM was fit to co-pyrolysis of biomass with plastics for PP, PETE, and BPC but for only one condition of plastic content (~50%) which is representative of most of the observed synergy. The objective function, which is also the average deviation function, was minimized to below ~3% for optimal fitting of the model to the experimental results. The fits seem good along with minimized error function. This model fitting provides 19 independent parameters: 5 average activation energies, 5 standard deviations of activation energies, 5 frequency factors, and 4 weight coefficients (5 parameters-1 constraint) for each of these conditions. All parameters obtained from these fits for all the conditions examined here are given in Table 8. In

comparison with the literature for pinewood parameters, the activation energy obtained here was lower (around ~ 115 kJ/mol). This was due to the multi-component analysis including 5 components unlike contemporary DAEM that has 3 components along with higher pre-exponential factor compared to that reported in the literature [126].

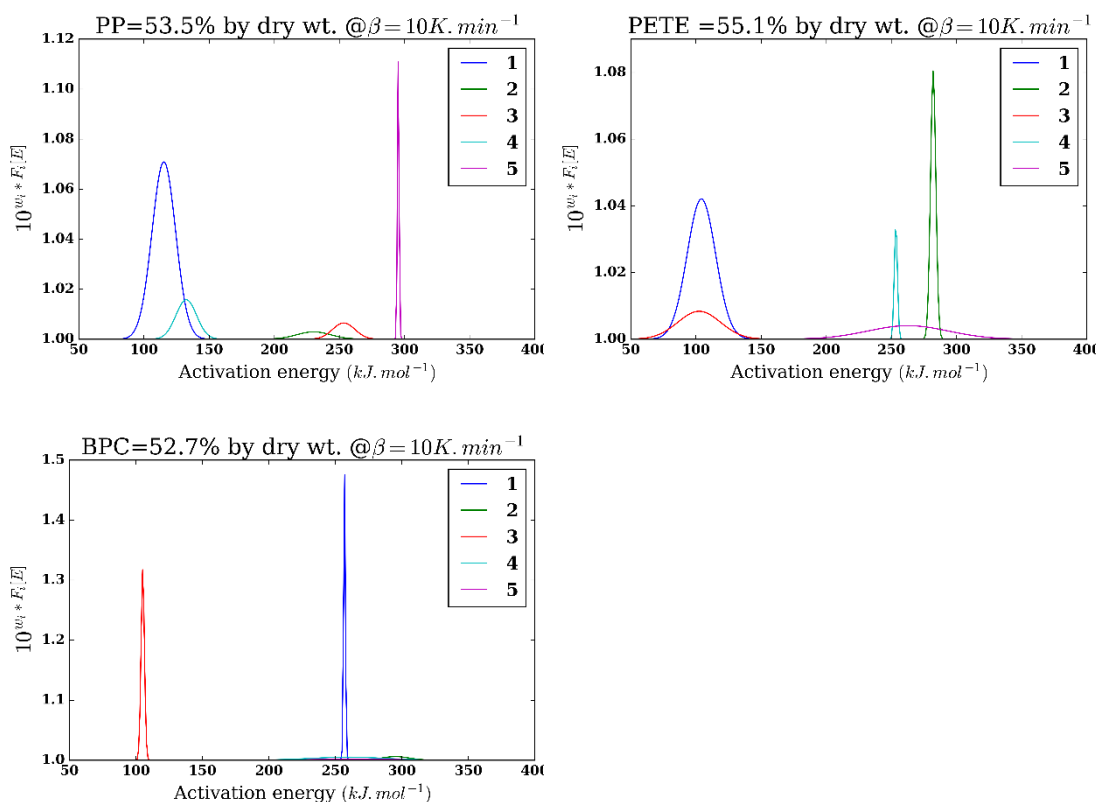


Figure 52. Weighted activation energy distribution from DAEM of co-pyrolysis at 10 K.min^{-1} (y axis in 10^x scale, and the legend represents the pseudo component). Top Left: PP, Top right: PETE, Bottom: BPC

To obtain further insights into capturing the synergistic effects through modeling using DAEM, weighted activation energy distribution plots were obtained which showed qualitative contributions of each of the pseudo components to the total reaction, as well as their activation energy distribution. This provided an ease of comparison between the individual and co-pyrolysis in a better way. Figure 51 shows the weighted activation energy distribution for individual component pyrolysis of PP,

PETE, BPC and pinewood. From these results one can see the number of pseudo component reaction sets that each material's DTGs can be deconstructed into. Lignocellulosic content usually needs three components, but here only 2 components contributed to major dimensionality of pinewood decomposition. PETE pyrolysis was unquestionably represented by only one pseudo component, while PP pyrolysis needed two, and BPC pyrolysis needed three. The requirement of two components for PP pyrolysis means that the pathway of PP involves two kinds of parallel reactions, which may be depolymerization of straight chains, and decomposition of cyclic oligomers formed via rearrangement. Only one component for PETE may mean that its pyrolysis was predominantly depolymerization along with dehydration and decarboxylation and the reverse reaction of char formation reactions and decomposition of char precursors was negligible. Three components required for BPC could mean three important degrees of BPC decomposition pathways. The chemistry based evidence and detailed insight need further spectroscopic analysis of the intermediate formation, but mathematically, these number of pseudo-components are sufficient to represent their individual component pyrolysis.

An examination can be made with similar plots for weighted distribution of activation energy for co-pyrolysis of pinewood with plastics (PP, PETE, and BPC) with plastic content maintained at ~50% (by wt.). Comparing these distribution plots for co-pyrolysis with individual component pyrolysis showed significant change in the dimensionality of the progress of pyrolysis.

Considering the co-pyrolysis PP with pinewood, major contributors to individual component pyrolysis in PP were sharp peaks at ~150 kJ/mol and ~290

kJ/mol while for pinewood the sharp peak was at 120 kJ/mol. But co-pyrolysis of PP with pinewood yields the distribution plot to have only one relatively sharp peak and the rest were four broadband peaks. The sharp peak of component 5, in PP co-pyrolysis in Fig. 52, was the same as the contribution from individual component pyrolysis of PP. But increase in the bandwidth of the peaks near 120 kJ/mol, that corresponded to pinewood pyrolysis (hemicellulose and cellulose contributions), with co-pyrolysis with PP is attributed to diffusion limitation caused by melted PP on the pyrolysis of biomass. Such melt layer may make it harder for the volatiles to escape, as proposed in [148], and thus increasing their residence times and interaction with the solid/melt phase components in the sample holder. This limitation also enhanced the contribution from the decomposition of lignin, which may be represented by either component 2 or 3. The significant mathematical insights gained from these plots enables one to hypothesize the synergistic reaction pathways that helps to improve understanding of the chemistry from intermediates/radical detection.

Comparison of PETE co-pyrolysis distribution results in Fig. 52 with individual component results in Fig. 51, reveals broadening of the biomass peaks, similar to that observed in PP co-pyrolysis. The explanation for broadening is akin to that of PP pyrolysis, which is from the PETE melt causing diffusion difficulties for the volatiles formed to escape and thus enhance their reactivity and PETE radicals formed earlier. A peculiar sharp and significant peak corresponding to component 4 and an enhanced broadband peak of component 5 refers to increase in the dimensionality of PETE pyrolysis when mixed with biomass. This sharp peak can be from the decomposition of intermediate radicals that form by volatiles interacting with PETE oligomers. On a

chemistry scale, the complexity of PETE and biomass pyrolysis increased non-additively compared to when pyrolyzed separately and the increased set of reactions are of decomposition of strong intermediates corresponding to the component 5 broadband, and a decomposition of highly reactive intermediates corresponding to component 4.

Co-pyrolysis of BPC with pinewood changed the distribution plot in a different way compared to PP or PETE with pinewood. Unlike the previous plastics, BPC co-pyrolysis did not significantly broaden the peak bandwidths. Instead, the peaks of 100-150 kJ/mol narrowed from BPC individual component pyrolysis and interacted with the peaks from biomass pyrolysis to collapse into a single sharp peak. Along with this, the sharp peak of BPC at 310 kJ/mol shifted to significantly lower activation energy of ~260 kJ/mol when co-pyrolyzed with pinewood. Of the tested plastics, only BPC's individual component distribution plot, shown in Fig. 51, has peaks that overlap with that of pinewood decomposition peaks. This leads to variation in significant mutually reacting pyrolysis that enhance the reaction rates by narrowing of the distribution peaks. Also, from Figs. 47-49, BPC co-pyrolysis with biomass showed significant enhancement in the pyrolytic behavior compared to other plastic-biomass blends. This provides an important conclusion that the overlap of temperatures in decomposition of biomass and plastic is not sufficient to have profound synergistic pyrolysis but overlap of distribution peaks in activation energy plane for the plastic and biomass are necessary for such chemically interactive synergistic effects.

The above results signify the important advantages of co-pyrolysis of biomass with plastic wastes. The kinetics study adds to the existing literature on the conversion

of individual components for fuel and energy production. The synergistic enhancement in both the efficiency of carbon conversion due to mutual interaction between biomass and plastic wastes was observed and quantified using DAEM. The DAEM proved to be an effective mathematical tool in transformation of TGA data into an activation energy distribution plane, which provided better insights into the pyrolytic behavior than direct comparison of mass loss or conversion along with providing mathematical deconvolution of synergistic behavior. Transformation of the DTG data of biomass and plastic pyrolysis into a distributed activation energy plane showed that interaction between PETE and biomass, and PP and biomass is majorly due to physical nature of the polymer and not from diffusion limitation. Co-pyrolysis with polycarbonate showed that such physical phenomenon was not the only way for the synergistic effects. Activation energy distribution of polycarbonate and biomass individual component pyrolysis overlapped so that when they were co-pyrolyzed, similar energetic sets of reactions interacted chemically and mutually to enhance their reaction. The enhanced kinetics due to synergistic behavior makes co-pyrolysis an effective pathway for thermochemical conversion of biomass and plastic wastes to produce clean energy. The degree of synergistic influence can be directly seen from the enhanced volatiles yield or carbon conversion from co-pyrolysis compared to individual component pyrolysis. Such degree of synergy can be summarized from the analysis of char residue reduction presented in Fig. 48 for different biomass-plastic blend ratios. Highest degree of synergy was observed with BPC plastic content of 50% for in pinewood, 75% for PETE in pinewood, and 25% for PP in pinewood. DAEM is a decomposition model and as such it excludes the intermediates or sequential reaction pathways that lead to

condensed phase species, such as char. Investigation of TGA studies to better identify possible co-pyrolysis pathways, by fitting the suggested simplified pathway to TGA data, as in ref. [156] provides a pathways for future research in this area. Inclusion of condensed phase species formation is critical if the DAEM was to be used in predicting char formation during co-pyrolysis. Our current efforts exclude char formation during co-pyrolysis, but rather additional gas species formation. Chemical intermediate speciation effects on the degree of synergy were not considered here and are therefore beyond the scope of this work but are considered necessary for future study to help analyze interaction between biomass-plastic blends. The kinetics analysis provides novel contribution in understanding the behavior of biomass-plastic mixtures, which is essential for the development of high efficiency, feed flexible pyrolyzer or gasifier for sustainable energy production from a wide variety of waste feedstocks.

Chapter 7: Deconvoluting Synergistic Interaction in Co-pyrolysis of Pinewood and Plastic Wastes

7.1 *Introduction*

Although existence of significant synergistic effects has been validated in the co-pyrolysis of biomass and plastic wastes, the detailed interaction mechanism is still not clear. Moreover, most co-pyrolysis investigations were conducted with the evenly mixed biomass-plastic blends. In the process of co-pyrolysis, interactions between volatiles, volatiles and unreacted feedstock, volatiles and char may all contribute to the observed synergy. The complex synergistic pathways make it challenging to clarify the contribution of each component to the overall synergy and elucidate the detailed synergistic mechanism via the uniform mixing co-pyrolysis scenario. Globally designed feedstock configurations to separate out the effects of volatiles and char, from each component, are needed to provide further insights into the synergistic effects in co-pyrolysis of biomass and plastics.

In this chapter, we investigated the co-pyrolysis of PS with pinewood in a fixed bed reactor equipped with product gas, and energy analysis using different feedstock mix configurations. Different configurations were used to reveal the interaction between volatiles-volatiles, volatiles-feedstocks, and volatiles-char to quantitatively provide the sources of interaction and their synergistic influence on the syngas yield, see Fig. 53. These plastics undergoes transition from amorphous to viscous melt phase before the start of degradation may hinder heat and mass transfer during the co-pyrolysis process due to its low heat transfer rate and weak diffusion [124,125].The

tests were carried out isothermally at 900 °C with focus on the feedstock characteristics. Evolution of product gas composition and mass flow rate were obtained along with the energy consumption to carry out these co-pyrolysis tests to reveal the impact of interaction on the syngas and energy efficiency characteristics. These tests provided with significant delineation of the co-pyrolysis of biomass with polystyrene and its synergistic effects. Considering the different monomeric structure, melt flow index, and char-forming nature of polycarbonate (PC) and polypropylene (PP) in comparison with PS, the co-pyrolysis of with these plastics may yield different physical and chemical synergistic behaviors. So, this will be followed by juxtaposing these results with deconvoluted studies on pinewood-PP and pinewood-PC co-pyrolysis, to provide insights into the impact of plastic class i.e., alkane based, carbonated aromatic, and substituted aromatic polymers on the synergy observed.

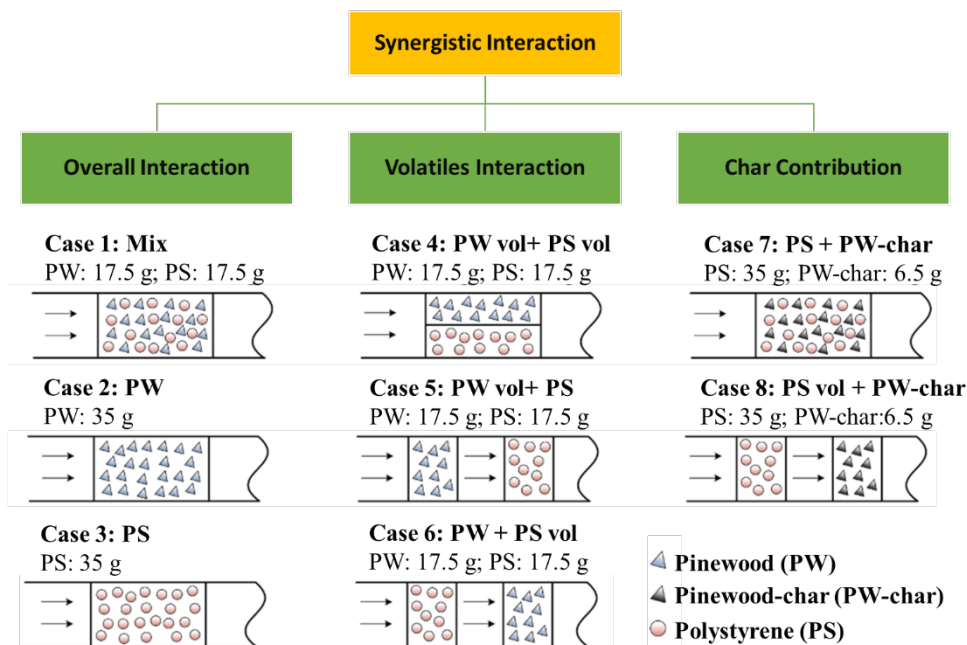


Figure 53. Different cases of feedstock arrangement for deconvolution of synergy in co-pyrolysis

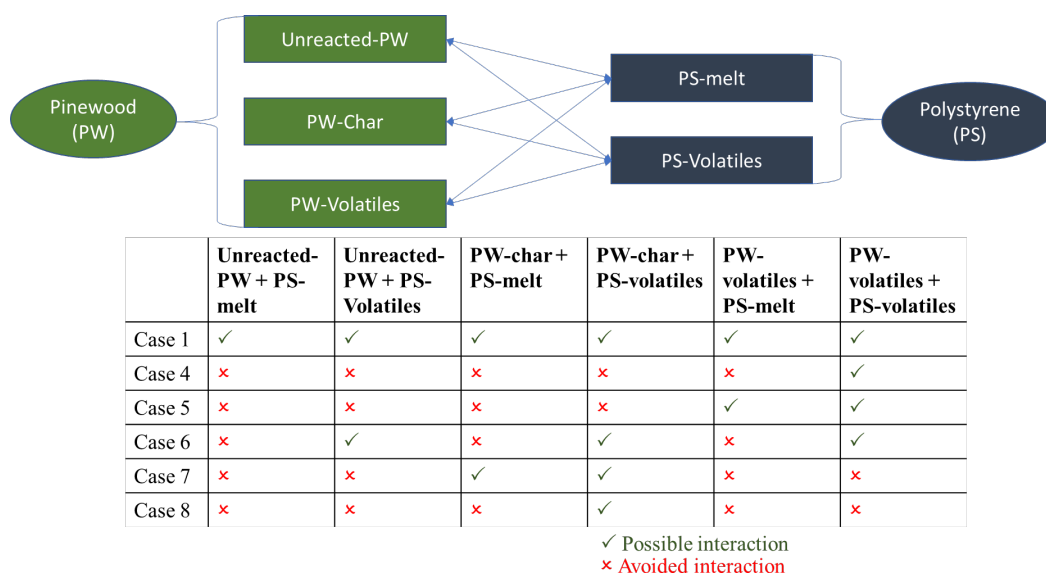


Figure 54. Simplified reaction model and synergistic pathways possible in different feedstock arrangement cases

For the deconvolution of interaction between different phases of intermediates evolved from biomass and plastics, we carried out multiple co-pyrolysis tests with different amounts of PW and PS in the sample holder with respect to each other. Figure 53 shows these different configurations of PW and PS along with the mass of the feedstocks used. Due to the lack of any char residue from PS, its intermediate groups included PS-volatiles and PS-melt only. The total pyrolytic feedstock mass for all the tests was 35 g, while the biomass to plastic mass ratio was kept as 1:1. Figure 54 summarizes the simplified synergy model and the separation of these sources of interaction using different feedstock arrangement cases given above. The implications of this assumption can be to miss out some more of the synergistic sources which are beyond the scope of this work while further studies can be carried out to incorporate these effects. The extent of synergy or inhibition on each of the parameters were

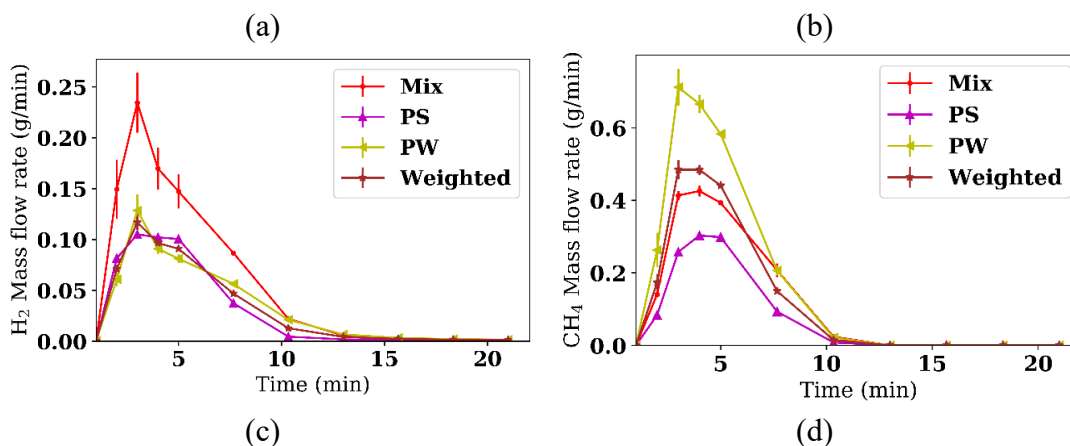
obtained as the percentage change with respect to the equivalent characteristics from the results of the weighted calculations.

In the cases of deconvoluting PW-PS and PW-PP mixtures, the mass ratio of PW to plastics was fixed at 1:1 (PW:17.5 g; PS: 17.5 g) for all their respective co-pyrolysis cases. The effect of PS char and PP char was neglected here because of insignificant charring from PS and PP pyrolysis, respectively. But in the case of co-pyrolysis with PC, effect of PC char was also carried out. Since 35 g of PW generated 6.5 g char and 35 g of PC generated 7.9 g char, 6.5 g PW char and 7.9 g PC char were utilized to understand the effects of char, such as Cases 7 and 8 in Fig. 53.

7.2 *Isolated synergies in the co-pyrolysis of pinewood and polystyrene blends*

7.2.1 **Cumulative synergistic impact of co-pyrolysis**

This section will initially examine the impact of interaction between evenly mixed PW and PS during co-pyrolysis since this represents the most common mixing pathway for co-processing. We will initially convey the impact of co-pyrolysis on the evolutionary behavior of syngas components followed by quantification of cumulative yield of these components along with the overall yield of syngas, char, and tar.



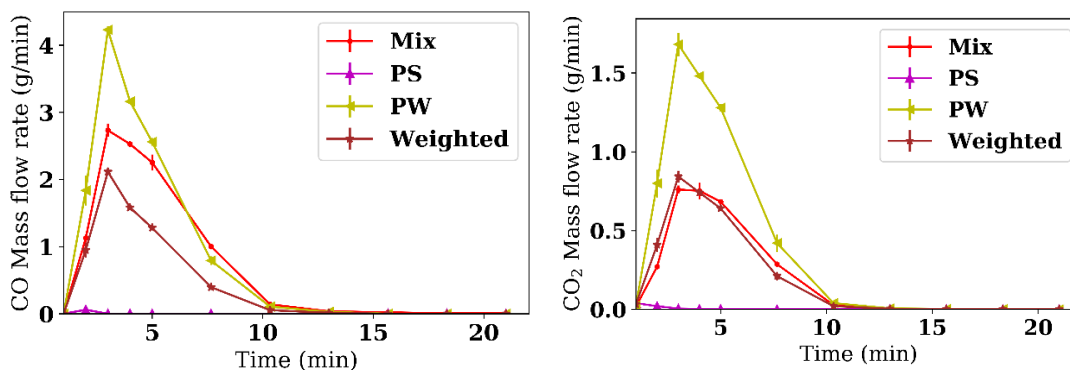


Figure 55. Temporal evolution of (a) H₂, (b) CH₄, (c) CO, and (d) CO₂ from co-pyrolysis of evenly mixed PW-PS blend

Figure 55 reveals the synergistic behavior in syngas components' evolution with time. H₂ evolution from PS and PW was similar in terms of the peak height, but the peak H₂ flow rate from PS seemed to be spread over 2-5 minutes from the start of pyrolysis while that from PW sharply peaked at 3 min. Comparing these results with the weighted behavior reveals significant increase in H₂ evolution in terms of both peak value and yield. This increase in H₂ flow rate was consistent with our previous studies involving co-pyrolysis of paper waste and PS [121]. Table 9 reveals the cumulative yield of individual syngas components over time for all the tested cases. Table 9 also reveals the enhancement in H₂ to go up from 0.6 g in weighted case to 1.14 g from co-pyrolysis due to synergistic increases. The kinetic behavior does not seem to be influenced via this synergy.

Table 9. Cumulative yields of syngas components and energy from different co-pyrolysis tests of PS and PW

	Mix	PW	PS	Weighted	PS-vol + PW-vol	PW-vol + PS	PS-vol + PW	PS + PW-char	PS-vol + PW-char
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	Case 1	Case 2	Case 3	(Case 2+ Case 3)/2	Case 4	Case 5	Case 6	Case 7	Case 8
H₂ (g)	1.14	0.67	0.60	0.63	0.89	0.82	0.99	0.59	0.97
CH₄ (g)	2.32	3.32	1.46	2.39	2.25	1.93	2.09	1.47	1.73
CO (g)	13.74	16.40	0.06	8.23	12.03	11.49	11.86	0.21	0.57
CO₂ (g)	3.90	7.58	0.06	3.82	3.77	3.65	3.51	0.14	0.11
C₂H₄ (g)	1.31	1.24	1.72	1.48	1.32	1.13	1.22	1.67	1.70
C₂H₆ (g)	0.12	0.15	0.13	0.14	0.14	0.12	0.14	0.12	0.15
C₂H₂ (g)	0.05	0.13	0.03	0.08	0.05	0.04	0.05	0.03	0.04
Ener gy (kJ)	461.5 2	484.0 6	233.9 6	359.0 1	411.9 2	371.3 3	409.3 1	232.4 7	298.4 8
Over all Ener gy Effici ency (%)	29.99	44.02	11.83	23.33	26.77	24.13	26.60	11.75	15.09

In contrast to enhanced H₂, the peak of CH₄ flow rate decreased during co-pyrolysis compared to weighted case. Figure 55(b) also reveals significant differences in the capabilities of PS and PW for CH₄ production. High CH₄ flow rates from PW pyrolysis corresponds to various sources including demethylation from methoxy and

acetyl groups, and breakdown of longer chains via thermal cracking of hydrocarbon oligomers [141,159]. But in the case of PS, high stability of its aromatic rings, along with the lack of easily removable methyl groups lead to CH₄ formation from sources that were limited to end chains and thermal cracking [114,160]. During co-pyrolysis, the cumulative decrease in CH₄ was only 3%, while the decrease in peak suggests its delayed evolution. The reason for this delay could be from the melt phase of PS causing diffusion-limitation in the evolution of species. A delay in PS decomposition was also observed when pyrolyzed with biomass in TGA [121]. So, the specific reason for this lowered kinetics in CH₄ needs further examination.

Due to the lack of any O content in PS, its CO and CO₂ evolution is negligible so that the source of these oxides is mainly from PW. A comparison of weighted and mix case shown in Fig. 55(c, d) reveals that the presence of PS has a positive influence on the evolution of CO yield from 8.2 g to 17.4 g, see Table 9. The enhancement in CO flow rate is consistent with our previous results [121]. While it may seem that the presence of PS enhanced CO evolution from PW, such enhancement is more possible from the O transfer from biomass intermediates to the hydrocarbon intermediates evolved from PS to produce CO. The CO yield can also be from the volatile-phase reforming of PS intermediates in the presence of CO₂ from biomass. Due to the lack of any significant change in CO₂ yield from co-pyrolysis, the impact of CO₂ based dry-reforming is probably more likely involved. So, the actual source and the pathway for this enhanced CO and O-transfer needs further examination.

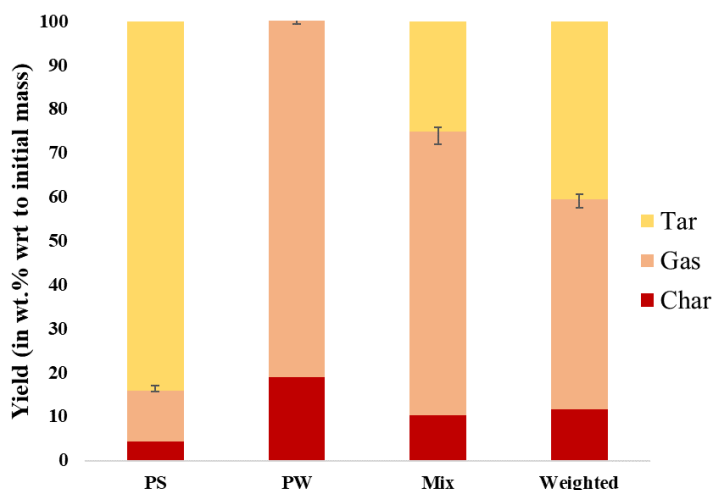


Figure 56. Comparison of the yields of gas, char, and tar from separate pyrolysis and co-pyrolysis of PS-PW (Mix)

Measurement of char from these tests was also carried out. The char yield in conjunction with the product gas yield was utilized to obtain tar yields (via subtraction). Figure 56 shows a comparison of the relative yields of gas, char, and tar products obtained from these tests. The results elucidate the overall impact of co-pyrolysis of PW-PS blends in terms of significant enhancement in carbon conversion to gaseous products and thus making co-processing more favorable for syngas production. At the high-temperature pyrolysis condition, the products from PW had no tar content which displays the favorable conversion of biomass to gas and char formation. In contrast, PS provided only ~11% gas yield and 4.4% char yield. Since most of the gas yield from PS was in the form of H_2 , CH_4 , and C_2 components, their source can be traced to be thermal cracking of PS volatiles. Thus, it reveals the high stability of volatiles from PS is due to high aromaticity and its favor to form cyclic compounds from their oligomeric form. Some of the most common products from PS pyrolysis are monomer, dimer, and trimers. After the initiation of its pyrolysis via random-scission, the oligomers are

proposed to undergo intermolecular and intramolecular H-transfer followed by β -scission to form these molecules [161,162]. These molecules at high-temperature can either undergo thermal pyrolysis to form coke and H_2 or recombine to form cyclic compounds in the form of tar. Catalytic pyrolysis studies of PS revealed that the carbon deposition on the catalyst, which led to its deactivation, was not filamentous carbon [163]. This suggests that, at least in the presence of catalyst, the cracking pathway to form coke and H_2 is more favorable. In our case, further analysis will be needed to understand their preference. In the presence of PW, the yield tar/coke decreased from 40% to 25%. Although this may still seem significant, in the perspective of gasifiers, this can be lowered by further reforming using gasifying agent as reported in our previous studies [121,164].

The increase in the syngas components also leads to improved energy yield and overall energy efficiency. Table 9 shows the energy yield and efficiency from the pyrolysis tests. The energy yield increased from 360 kJ to 460 kJ via co-pyrolysis which accounts for increased overall efficiency from 23% to 30%. The efficiency levels are low due to the lab-scale operation and establishing improvement at this scale can help in improving the industrial scale realization of this process. For this, further understanding of the pathway for improvements found in this interaction and any potential inhibition is important.

Based on our simplified grouping of the intermediate species from PW as volatiles, unreacted, and char, while those from PS as PS-melt and volatiles, synergistic influence in co-pyrolysis can arise from 6 possible interactions between these component groups. The different configurations of feedstock arrangement as shown in

Fig. 54 were carried out to isolate the impact of these 6 interaction. This section further explores each of these interactions and their contribution to the interaction between PW and PS in the increasing order of complexity from these tests using different configurations.

7.2.2 Deconvoluted interaction between PW-char and PS-melt

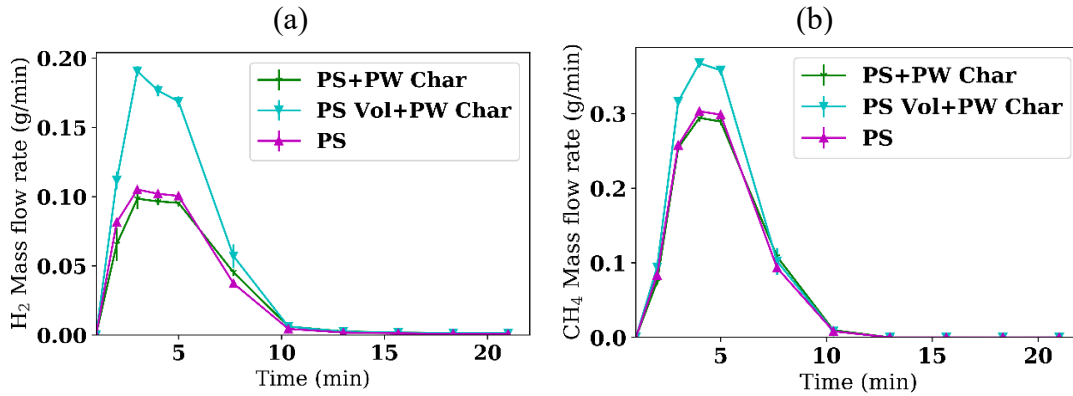


Figure 57. Evolution of (a) H₂ and (b) CH₄ mass flow rates from pyrolysis in cases 3,7 and 8

An understanding of the impact of interaction between PW-char and PS-melt can be obtained from comparing Cases 3, 7, and 8. Figure 57 shows this comparison for H₂ and CH₄ flow rates with time which reveals that the difference between PS pyrolysis and PS+PW-char pyrolysis is negligible. Similar behavior was found in our previous studies of evenly mixed plastic feedstock with biochar [129,165]. PS melts form early in the heating process and as the PW-char is stable and porous, the melts propagate to cover the char surface. Due to the low thermal conductivity and diffusion rate through this melt phase, the pyrolysis continues from outer layer while the pyrolysis at the interface between char and melt is delayed [138]. This mechanism would mean that the impact of PW-char on the PS decomposition is minimal, especially

with respect to syngas components as majority of these from PS form away from the decomposing melt-phase.

Some enhancement in the yield of CO and CO₂ was found in these cases, see Table 9. The O content in PS is very low and limited to only some peroxide linkages. It means that these species and their enhancement could have either come from reaction between the O content on the surface of PW-char with PS-melt, or from some intake of atmospheric oxygen during the insertion of sample holder into the reactor. The latter is more plausible as the evolution rates of CO and CO₂ in these cases is very fast and mostly occurs in first 2-3 minutes. This is a limitation of the experiments and the net molar carbon loss in this regard is minimal so that no further discussion will be made here in this regard.

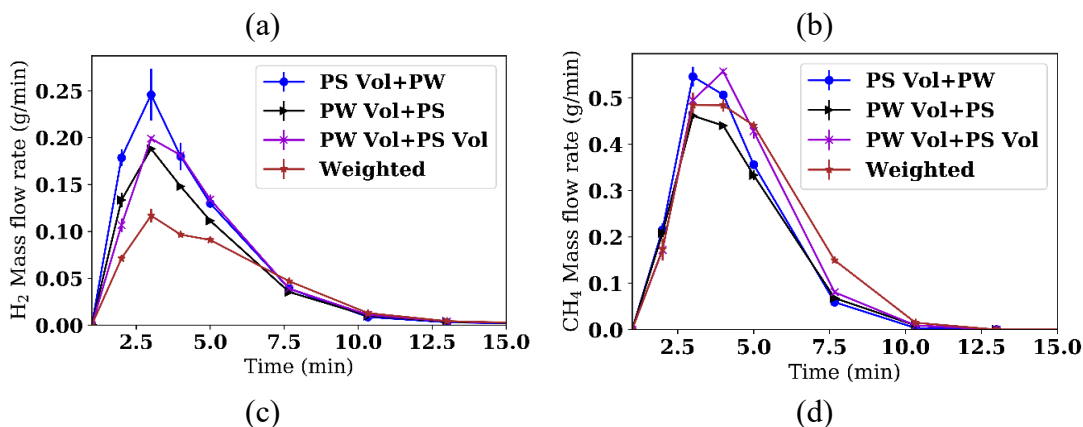
7.2.3 Deconvoluted interaction between PW-char and PS-volatiles

The impact of this interaction can be obtained by comparing the Cases 3, and 8 given in Fig. 54. As the contact between PW-char and the PS-melt was avoided by placing quartz wool between them while allowing for the PS-volatiles to react with PW-char, the inhibitive behavior of PS-melt on PW-char was avoided. This results in clear revelation of the catalytic impact of PW-char on thermal cracking of PS-volatiles. Figure 57 reveals this catalysis resulting in improved H₂ and CH₄ flow rates. This catalytic behavior is due to the active surface area of PW-char towards catalytic cracking of the PS-volatiles. Such behavior was also reported in the literature involving catalytic pyrolysis of plastic wastes using biochar and our previous studies involving plastics such as PP and PC [129,165,166]. H₂ and CH₄ cumulative yields improved from 0.6 g and 1.5 g to 1g and 1.7 g respectively, see Table 9. The catalytic influence

on C₂ components was minimal as shown in Table 9, due to the lack of significant sources for C₂ gases from PS pyrolysis. This contrasting influence of PW-char on PS-volatiles and PS-melt suggests the importance of controlling the contact between the intermediate groups of different waste components.

Table 9 also reveals an increase in CO yield from PS-volatiles interaction with PW-char. Unlike the case of PS-melt interaction with PW-char, here the CO flow rate was found to be higher over longer time duration. This suggests that, in addition to possible atmospheric oxygen based error, PS-volatiles also interacted with PW-char's O content to form CO. Even with this increase, the CO is very low, since it is limited by the available oxygen. It also suggests that thermally stable PW-char can be slowly deoxygenated in the presence PS-volatiles. These results are of potentially significant importance in co-gasification applications as this char's catalytic influence is also competing with its reaction with the gasifying agent.

7.2.4 Deconvoluted interaction between PW-volatiles and PS-volatiles



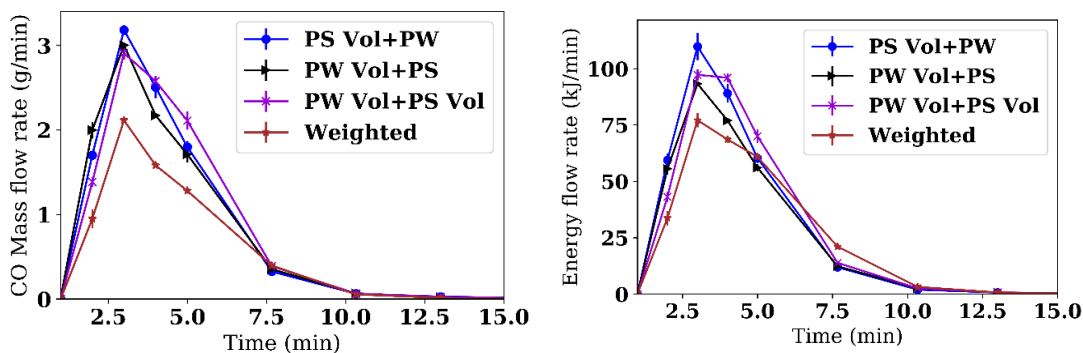


Figure 58. Evolution of (a) H₂, (b) CH₄, (c) CO and (d) syngas energy flow rates during volatile interaction-dominated tests in co-pyrolysis of PW and PS [x-axis zoomed for clarity in the comparison]

In addition to these char effects presented earlier, interaction between the volatiles from PW and PS in gas-phase secondary reactions can also have significant impact on the synergistic product behavior [167]. Feedstocks' arrangement in Case 4 (PW Vol + PS Vol) can isolate this interaction from the other possible routes for providing direct quantification of its influence on syngas evolution. Figure 58 shows a comparison of this case with the weighted case for this quantification.

Figure 58(a) reveals the H₂ evolution from volatiles-volatiles interaction to be significantly different, with peak flow rate almost doubled along with relatively faster rate. Table 9 reveals the quantified cumulative yield of H₂ to increase from 0.63 g to 0.89 g which means a synergy of 40% increase due to this interaction. While various pyrolysis studies have acknowledged the influence of secondary reactions to the product output, its influence and contribution to synergistic effects is lacking in the literature. Our previous studies revealed volatile-volatile interaction to provide synergistic increase of H₂ yield by 20% [165]. As the volatiles from PS pyrolysis such as styrene and its oligomers evolve, they can react with the reactive oxygenated volatiles from PW such as furfural, acetic acid, phenolics, levoglucosan, along with

CO₂ and H₂O to undergo a mutual H-transfer from the PS-volatiles to O-transfer from the PW-volatiles [168,169]. Oxygenated volatiles then undergo thermal cracking to further reform into H₂ and CO. Figure 58(a, c) validates this pathway with a significant increase in the peak of CO flow rate. The cumulative synergy in CO accounts to 46% enhancement. Similar extent of enhancement in CO and H₂ confirms that most of this synergy is sourced from reforming reactions.

Comparing the CH₄ evolution in Fig. 58(b) reveals a shift towards lower pyrolysis times compared to the weighted case. This suggests an improvement in the kinetics of CH₄ production via volatiles interaction while the change in CH₄ yield was minimal (a decrease by 5%). Improved reforming reactions and availability of reactive O countered by relatively higher stability of CH₄ can account for such a mild decrease. The H and O transfer between volatiles can also account for this earlier evolution of CH₄, as it leads to lowered intermediates stability and improved cracking to lower chain lengths. Synergy in the yield of C₂ components was also similar to CH₄ which suggests an earlier breakdown of the volatiles.

The changes in these components contributed to an increase in syngas by approximately 21%, as seen from Table 9. This also means a decrease in the carbon loss from PS to tar and coke by-products. Hence, this volatiles interaction inhibits recombination and aromatization reactions to further their breakdown into syngas components. Figure 58(d) also shows an improved syngas energy production (calculated based on the LHV of individual syngas components) due to volatiles interaction. This enhancement accounts to a synergy with 15% increase in the energy yield, from Table 9. These results not only provide novel quantified results of the

impact of volatiles interaction, but also reveal its potential to favor syngas production. Ex-situ catalysis can improve these interaction to further enhance the quality of products, while the decrease in coking tendency of plastics via this route means, a better catalytic performance [90].

7.2.5 Deconvoluted interaction between PW-volatiles and PS-melt

During co-pyrolysis of PW and PS, the evolving PW-volatiles can interact with both PS-volatiles and PS-melt groups. The interaction with PS-volatiles was discussed in the previous subsection. We now focus on its interaction with PS-melt. A combination of both these interactions is possible in Case 5 configuration, wherein the PS is placed downstream of PW without any direct contact between the solid/melt phases. Comparing the synergy obtained from this case with volatiles interaction (Case 4) can reveal the net contribution of the interaction between PS-melt and PW-volatiles. Figure 58 shows this comparison between volatiles-volatiles and volatiles-feedstock cases for the evolved H_2 , CH_4 , CO , and energy flow rates. The results reveal that H_2 flow rate from both the cases is almost identical until 3 minute mark, after which the PW Vol+PS resulted in lower H_2 flow rate than PW Vol+PS Vol. This is unlike our previous results involving PW and PC, while the studies with PP showed a decrease in H_2 flow rate [129,165]. This decreased behavior after 3 minute mark was also observed in CH_4 and CO flow rate. This led to retention of such behavior on energy flow rate. The synergy observed from Case 5 was 28.7% increase in H_2 , and 39% increase in CO yields while decreasing CH_4 yield by 19%, from the data shown in Table 9. Case 4 reveals that the volatiles interaction can increase H_2 by 40%, CO by 46% and decrease in CH_4 by 5%. This means that the interaction between PW-volatiles and PS-melt led

to the difference between Case 4 and 5 which resulted in decreased H₂, CH₄ and CO production.

Possible explanation for such inhibitive behavior can arise from a phenomena akin to absorption or dissolving of the PW-volatiles in PS-melt phase. This can result in the loss of some of the syngas-destined volatiles to get trapped in PS-melt to result in decreased syngas yield. This decrease, in comparison with volatiles-volatiles case, arises only after the 3 minute mark. As the temperature of PW increases, it releases different types of volatiles. It suggests that the volatiles that form after this time duration are more prone to interact with PS-melt and cause loss of syngas.

Another explanation could be from the inhibition of PS decomposition by PW-volatiles by causing transport limitations around PS-melt and result in increased recombination reactions. But the decrease in all the components including CO and CO₂, which mainly arise from PW-volatiles, makes this explanation less plausible compared to the former. The inhibition of PS decomposition may not necessarily cause CO and CO₂ loss, but this interaction can result in O-transfer from PW-volatiles into PS-melt without the H-transfer to result in a combination of more stable intermediates in PS-melt. So, the interaction between unreacted-PS or PS-melt and PW-volatiles needs to be minimized, as much as feasible, to efficiently utilize the synergistic interaction between these feedstocks.

7.2.6 Deconvoluted interaction between PS-volatiles and unreacted-PW

The different configurations utilized for these co-pyrolysis tests cannot directly delineate the interaction between the PS-volatiles and the unreacted-PW. Here, unreacted-PW refers to the group of intermediates in solid-phase that were yet to

convert to char or evolved volatile phases. Understanding the interaction between these groups can provide the influence of PS-volatiles on the initial decomposition of PW, and possible changes to the reactivity of PW feedstock to change its syngas production behavior. When PS-volatiles interact with pyrolyzing PW, this interaction can be split into reactions with PW-volatiles, PW-char, and unreacted-PW. As the quantitative influence of the former interactions are described above, this makes it easier to understand the interaction with unreacted-PW retrospectively, by comparing results from Case 4 (PS Vol+PW Vol), and 6 (PS Vol+PW) with the weighted results while considering the influence of PS-volatiles-PW-char interaction shown in Figure 57.

These results are provided in Fig. 58, which reveals that flow rates of H₂, CH₄ and CO are considerably higher in the PS Vol+PW case. This is because, in this configuration, all the 3 intermediate groups of PW can react with PS-volatiles and this cumulatively adds up to provide a significantly higher synergy with respect to the weighted case. Comparing H₂ flow rate from Cases 4 and 6 reveals their differences to be limited to the first 4 minutes wherein the Case 6 has higher H₂ flow rate. After 4 minutes, these differences are negligible. Figure 57 shows that the influence of PW-char on PS-volatiles stays until the 10 minute mark, while this is missing in Case 6. This is because Case 6 has lower char quantities that are catalytically ready to enhance PW-volatiles conversion as the PW is also simultaneously decomposing. The net synergy from this case was to increase H₂ yield by 55%, and CO yield by 44% while decreasing CH₄ by 13%. From previous section, we can see that volatile-volatile interaction contributed to 40% increase H₂, 46% increase in CO and 6% decrease in CH₄ yields. Here the % values are with respect to weighted case. Comparing these

results suggests that a significant portion of the interactions in Case 6 arise from synergy between PW-volatiles and PS-volatiles. The catalytic influence of PW char was to increase H₂ yield by 63%, and CH₄ yield by 18%, calculated from Table 9. Additionally, the net difference between energy yield from Case 4 and 6 was minimal. Considering these results together suggests that the interaction between PS-volatiles and unreacted-PW led to a relatively lower synergistic enhancement than anticipated.

One of the possible reasons for this behavior could be due to the arrangement of PS and PW. As the PW is downstream of PS, PS-volatiles first react with a combination of PW-char and unreacted-PW before meeting PW-volatiles. The solid-phase PW groups interacted with PS-volatiles to improve the net H₂ yield, and decrease CH₄ and CO yields, based on the differences between the synergy from Case 4 and Case 6. Juxtaposing this with the catalytic tendency of PW-char to improve H₂ and CH₄, we can postulate that the interaction between PS-volatiles and unreacted-PW causes decreased CH₄ and CO yield while the influence on H₂ is unclear as it increases in both the cases. PS-volatiles, when reacting with unreacted-PW, may inhibit the decomposition of PW which is the main source of CH₄ and CO. This could be from the transport limitations caused by these aromatic volatiles by blocking the evolution of PW volatiles from unreacted-PW. Additionally, PS-volatiles tend to coke, as shown in catalytic pyrolysis results, especially on reactive porous surface which is available on the solid-phase PW in the form satellite zones of PW-char [163,170]. So, the coke deposition from PS-volatiles on the unreacted-PW could also have led to this blocking to decrease the net synergy, while the PW-char catalytically enhanced this coking process to improve H₂ and CH₄ yield, which is also reported in the literature. Thus, the

interaction between PS-volatiles and unreacted-PW, similar to the interaction between PW-volatiles and PS-melt, is inhibitive. It means that the contact between volatiles and unreacted groups of the feedstock needs to be avoided to maximize the synergy between biomass and plastics during co-conversion processes.

7.2.7 Deconvoluted interaction between unreacted-PW and PS-melt

The above subsection reveals the influence of interaction between various intermediate groups from PW and PS during co-pyrolysis. The interaction between PS-melt and unreacted-PW is the most difficult to delineate using the feedstock arrangements utilized. Of all the cases, this interaction is possible only in the Mix case (Case 1) along with other interactions given above. So, using the above understanding of various interaction pathways and deducting their influence, we can expose this influence on the interactions.

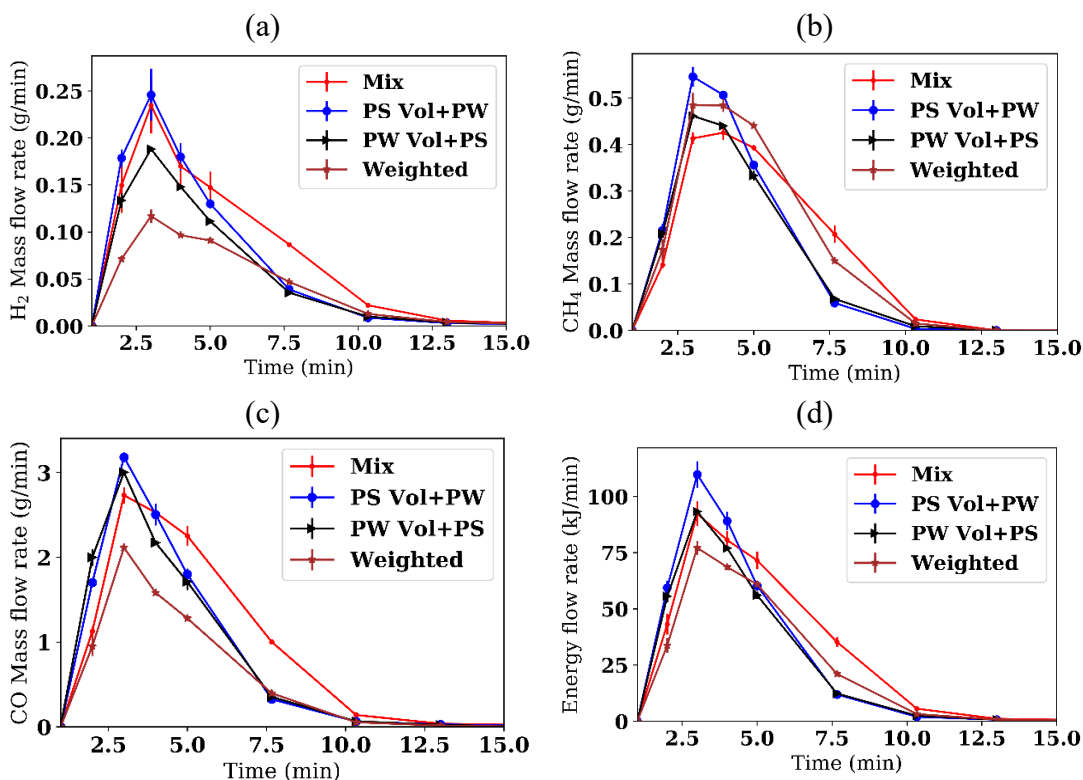


Figure 59. Evolution of (a) H₂, (b) CH₄, (c) CO, and (d) Energy flow rates from Cases 1,5,6 during co-pyrolysis of PW and PS

In Mix case, various interaction pathways are possible that includes: PW-volatiles+PSvolatiles, PS-melt+PW-char, PS-volatiles+PW-char, PS-volatiles+unreacted-PW, PW-volatiles+PS-melt, and PS-melt+unreacted-PW, see Fig. 54. Our understanding from previous subsections suggests that, as the PS-melt is in contact with the PW-char, the interaction between PS-volatiles and PW-char is inhibited in the Mix case. So, the influence of both these pathways is negligible. Thus, we need to compare the Mix case with PS-volatiles+PW, PW-volatiles+PS, and weighted cases to reveal the contribution of PS-melt+unreacted PW.

Figure 59(a) compares these cases to reveal that, until 4 minute mark, the Mix case, and the PS-volatiles+PW provided same H₂ flow rates which are higher than that from PW-volatiles+PS. After this, the Mix case yielded higher H₂ flow rates than the rest. The case of PS-volatiles+PW can have relatively higher tendency for H₂ that is not present in the mix case because this case lacks the inhibitive behavior of PS-melt and thus exposes catalytic behavior PW-char. The delayed behavior showing higher flow rates at later times was also present in CH₄ and CO evolution rates which carries over to the energy flow rate behavior, see Fig. 59(b, c, d). This delayed behavior was also mildly present in our PW+PC and PW+PP studies which revealed significantly longer time duration for completion of pyrolysis in the Mix case.

This delay suggests the capability of PS-melt to block unreacted-PW's conversion due to its low thermal conductivity. As the PS-melt also decomposes at relatively higher temperature, more unreacted-PW can convert to char and volatiles.

Due to the difficulty in separating out the interaction between PS-volatiles and unreacted-PW, using the PS-volatiles+PW case in comparison with other cases, this difficulty extends to not allow yield based on quantitative deconvolution of interaction between PS-melt and unreacted-PW. The net synergistic increase in H₂, CH₄ and CO is by 80%, -3% and 67% respectively from Mix case, compared to 55%, -12%, and 44% respectively from PS-volatiles+PW, and 28.7%, -19%, and 40% respectively from PW-volatiles+PS. As both these latter cases decrease CH₄ significantly compared to only a minimal decrease in Mix case, we can suggest that the interaction between PS-melt and unreacted-PW favors CH₄ production. Clear understanding of this interaction is still lacking and further studies into solid-solid and solid-melt interaction, possibly via in-situ FTIR are necessary to understand this behavior [171]. But in the perspective of improving co-pyrolysis and co-gasification, the temporal differences given above suggests an inhibitive behavior in terms of the kinetics during this interaction and thus should be averted in the case of PS-PW blends.

7.3 *Isolated synergies in the co-pyrolysis of pinewood and propylene blends*

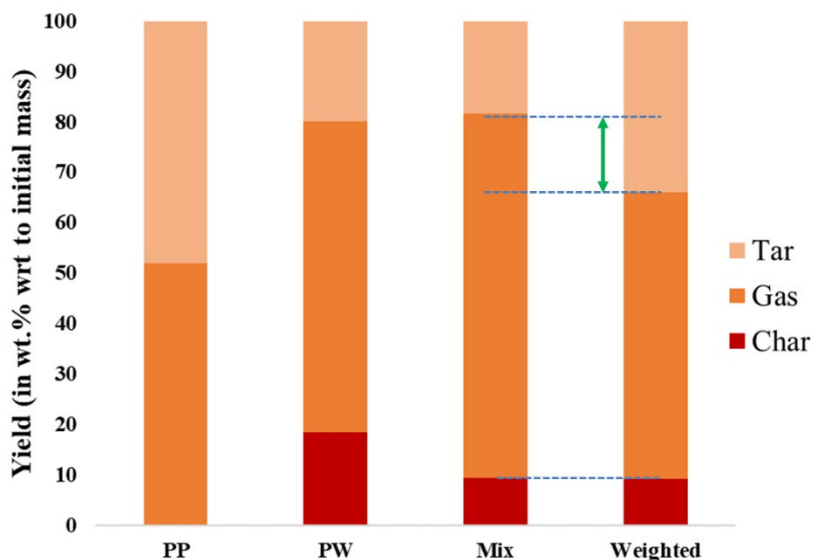


Figure 60. Comparison of the yields of gas, char, and tar from separate pyrolysis and co-pyrolysis of PP-PW (Mix)

In this subsection, we will discuss similar deconvolution techniques used to understand the synergy between PW and PP during their co-pyrolysis. Only brief results are shown here to add to the PW-PS cases and further details can be found in our co-authored article [165]. As in co-gasification studies done earlier, co-pyrolysis of PW-PP also led to synergistic enhancement of product gases at the cost of reducing tar by-products, see Fig. 60. But no significant change of char yield was observed from co-pyrolysis which could be from the lack of overlap in pyrolysis temperature range of PW and PP as observed from the TGA results, see chapter 4, and 6. Further details can be seen using the evolutionary details of these cases for individual components of syngas such as H_2 , CO , and C_nH_m (C_1 and C_2) flow rates.

(a)

(b)

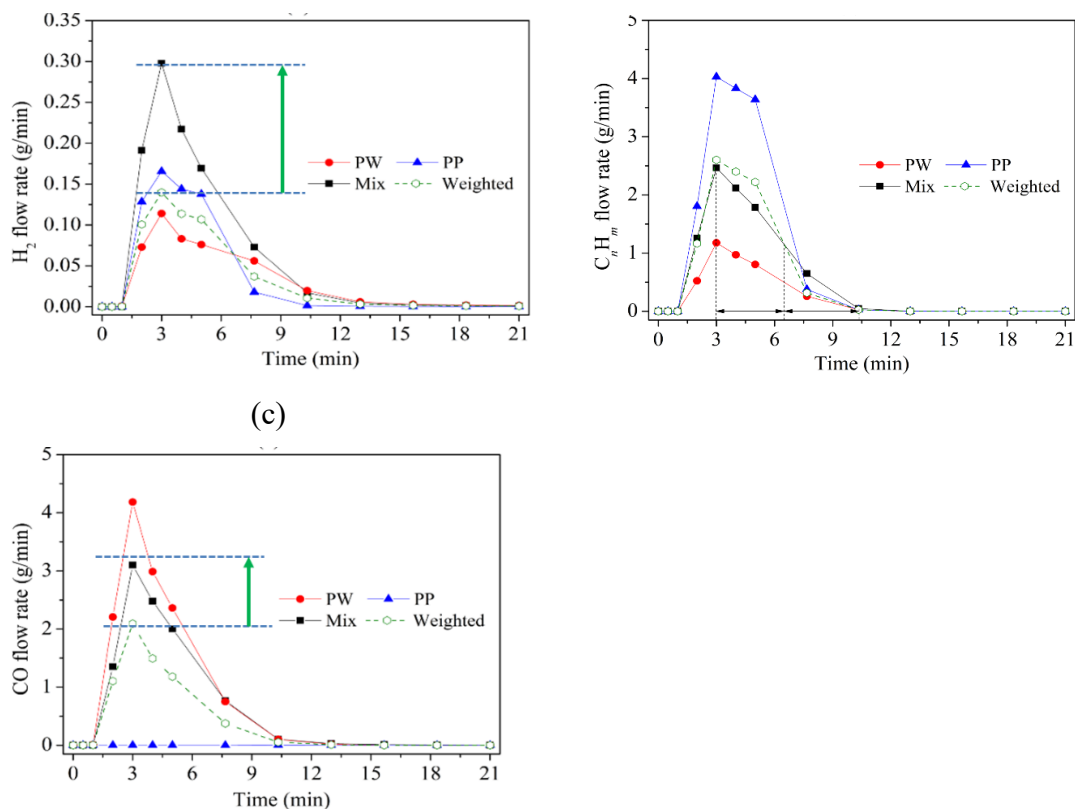


Figure 61. Evolution of (a) H_2 flow rates, (b) gaseous hydrocarbon flow rates, and (c) CO flows rates from co-pyrolysis and individual pyrolysis of PW and PP

Figure 61(a) shows the evolution of H_2 flow rates for co-pyrolysis and individual pyrolysis cases. A wider H_2 evolution for PW compared to PP was also observed here. The H_2 flow rates peak value was greater in PP case due to the higher hydrogen content in PP compared to PW. The peak H_2 flow rate of co-pyrolysis case was more than twice than that from weighted value when pyrolyzed separately. Similar synergistic enhancement was observed in the evolutionary behavior of CO, see Fig. 61(c). Figure 61(b) illustrates the evolution of gaseous hydrocarbon (C_nH_m consisting of CH_4 , C_2H_2 , C_2H_4 , and C_2H_6) flow rates from co-pyrolysis of the PW+PP mixture and the corresponding individual pyrolysis as separated feedstocks. Due to the absence of oxygenates in PP, there was no CO yield but much higher C_nH_m yield during PP

pyrolysis. The peak C_nH_m flow rate of PP was almost four times that of PW. However, the co-pyrolysis of PW+PP mixture did not show apparent synergistic enhancement on C_nH_m yield but suggested a delayed release of C_nH_m . Comparison of co-pyrolysis and the weighted value from individual pyrolysis showed a remarkable delay on syngas evolution due to this delay in C_nH_m release from PP. The time required for 95% of syngas evolution in PW+PP mixture was 8.9 min, which was 0.9 min longer than the weighted value, and 0.4 min longer than the pure PW case [165]. During the co-pyrolysis of PW and PP, the decomposition of PW started at a much lower temperature than PP, but the slow charring reactions of PW were still processing in parallel with PP decomposition [147]. So, the interactions between these PW char and PP melt may be responsible for the observed evolution delay.

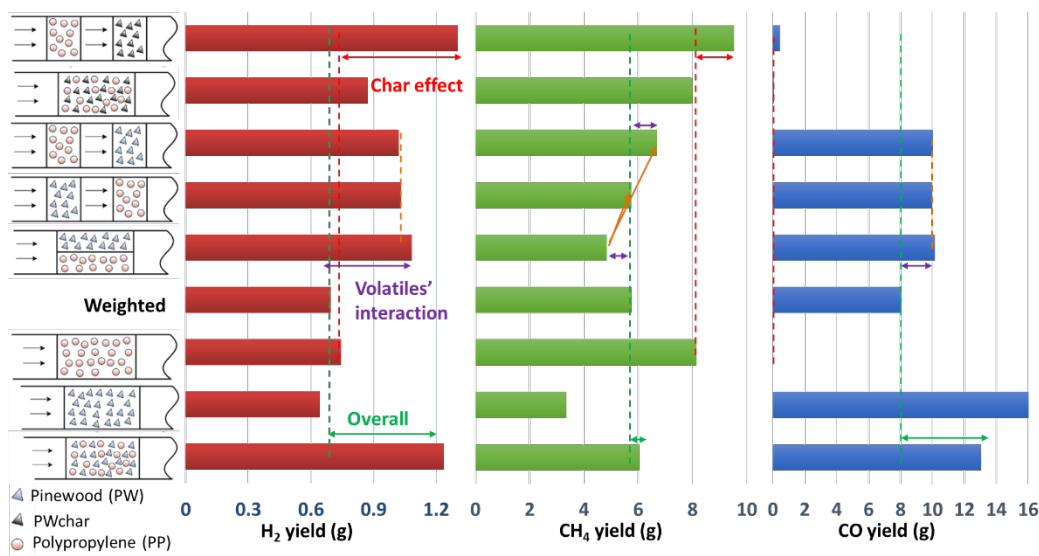


Figure 62. Cumulative yields of H_2 , CH_4 and CO from different feedstock arrangements of PW and PP

To further understand these effects, the cumulative yields of H_2 , CO , and CH_4 are provided for the different feedstock arrangements. Figure 62 depicts the cumulative

yields of H_2 , CH_4 and CO from co-pyrolysis and individual pyrolysis of PW and PP from different feedstock arrangement cases. The total syngas yield, H_2 yield and CO yield in co-pyrolysis were enhanced while C_nH_m yield seemed relatively unaffected with the synergistic effects. A remarkable enhancement in CO yield with only slight decrease in CO_2 during co-pyrolysis of PW+PP mixture can indicate that the hydrogen rich radicals (H and hydrocarbon radicals) from PP pyrolysis could have reacted with the CO_2 from PW pyrolysis for this CO_2 decrease.

From Fig. 62, volatiles mutual interactions exhibited much higher H_2 , and CO yields while decreasing C_nH_m yields than the weighted values, but lower than the evenly mixed co-pyrolysis case. This result indicates that the mutual interactions between volatiles originating from PW and PP provide positive contribution to the synergistic enhancement of H_2 yield. The co-pyrolysis of PW and PP facilitated the cross H-abstraction reactions between biomass volatiles and polymer volatiles to promote radical generation, which enhanced oligomers cracking with increased H_2 yield [118]. On the other hand, the degradation of high hydrogen content of PP released hydrogen rich radicals (H and hydrocarbon radicals), which acted as H-donor for PW volatiles with suppressed condensation and repolymerization reactions, resulting in the decreased tar formation while enhancing gaseous components conversion [172]. While further discussion can be found in the paper, it shows similar volatiles led synergistic enhancement in H_2 , and CO at the expense of hydrocarbons found in PW+PS cases.

Figure 62 also shows that the H_2 yield from volatiles interaction was relatively higher in comparison to volatiles-feedstock interaction cases, while CO yield was unchanged. Among these cases, CH_4 yield was highest for PP_PW case, possibly due

to catalytic enhancement of cracking of PP volatiles on PW-char, an effect that was absent in the volatiles' interaction case. This was similar to PW+PS case, but here, only CH₄ increased. This could be because in the case of PW+PS, the decomposition temperature ranges of PW and PS differ significantly and this means, most of the PW char is formed and catalytically active by the time PS volatilizes and thus allows for effective cracking. But in the case of PW+PP, this difference in decomposition temperature range is smaller and due to different heating rates of the feedstocks, the PW char is not fully formed to provide the catalytic enhancement to its fullest potential as shown in the figure. In addition, the interactions between PW volatiles and PP melt promoted C_nH_m formation, which was mainly due to the enhancement of PP degradation by radicals released from PW decomposition with low stability. Arrangements with a separation between the feedstocks provided faster kinetics in comparison to evenly mixed cases, possibly from the inhibitive behavior of plastic melt to delay the decomposition as observed in PW+PS cases.

It is reported that alkali and alkaline earth metals (AAEMs) presented in biomass char and the porous biochar structure had great catalytic effects on cracking reactions during pyrolysis [173]. It can be observed from Fig. 62 that the co-pyrolysis of PP and PW char with evenly mixed configuration results in only a slight H₂ increase while maintaining a separation between these to ensure no PP-melt's blocking behavior ensured significant increase in H₂ and CH₄ yields. Similar to PW+PS case, the pyrolysis of PW initiated at a much lower temperature than that of PP, which resulted in the coexistence of PW char and PP melt during the co-pyrolysis of PW+PP mixture. The porous structure of PW char was easily blocked by the fused PP, which hindered the

contact of PW char with evolved PP volatiles. Thus, the catalytic effect of PW char was minimized during the co-pyrolysis of PW+PP mixture. Moreover, the PP melt that existed in char holes was pyrolyzed at a relatively low reaction rate because of the poor heat conductivity, which resulted in the delayed C_nH_m and syngas evolution during co-pyrolysis.

7.4 *Isolated synergies in the co-pyrolysis of pinewood and polycarbonate blends*

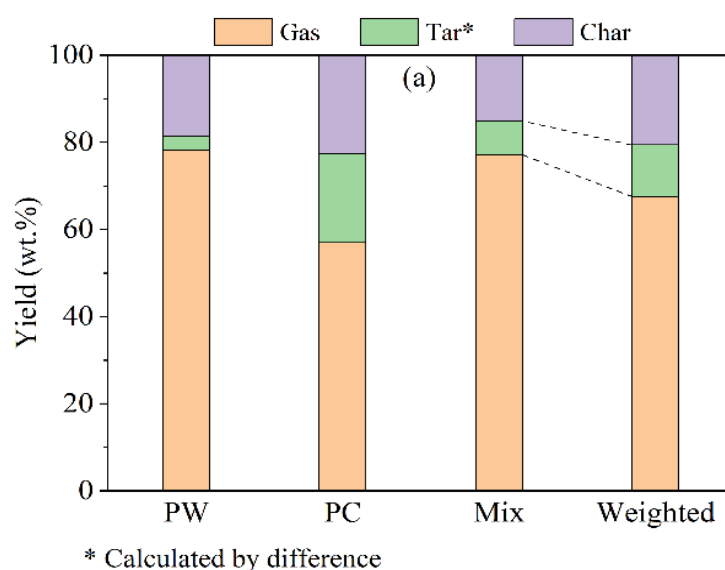


Figure 63. Comparison of the yields of gas, char, and tar from separate pyrolysis and co-pyrolysis of PC-PW (Mix)

Similar to PW+PS and PW+PP, the deconvolution of co-pyrolysis of PW+PC mixtures was also carried out and the results are published in co-authored papers [129,174]. Figure 63 shows the comparison of relative product yields from co-pyrolysis of evenly mixed PW-PC mixtures with weighted results. Tar considered here referred to all condensable vapors including water, which was measured by subtracting the char and gas yields. Similar to steam gasification results, co-pyrolysis led to increase in

product gas yield while decreasing tar and char yields. This indicates that the synergistic effects in co-pyrolysis of PW and PC not only involved mutual interactions of volatiles to occur in gas phase, but also included volatiles-solid interactions towards enhanced conversion to gases. The overlap between decomposition temperatures of PW and PC as seen in chapter 4 and 6 could be the reason for this significant char reduction, possibly from solid-solid interactions between unreacted-PW and PC-melt where the ester bonds of PC could help in reacting with the decomposing PW sites.

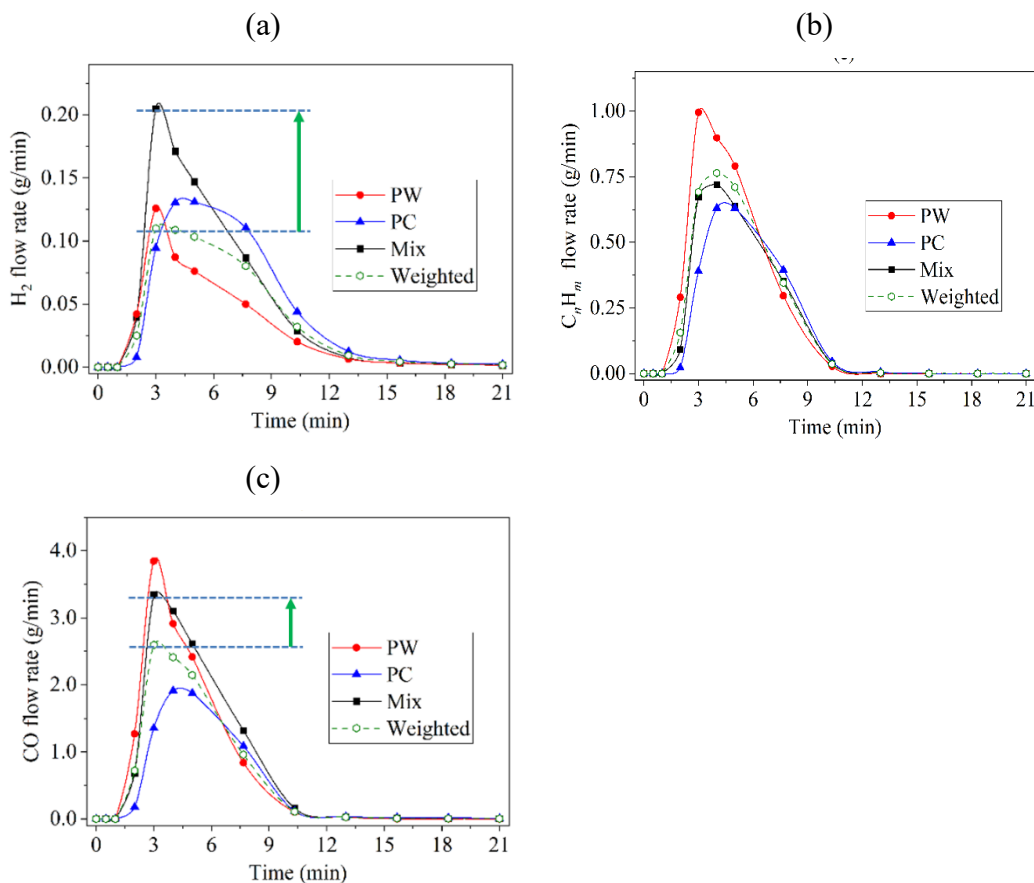


Figure 64. Evolution of (a) H₂ flow rates, (b) gaseous hydrocarbon flow rates, and (c) CO flows rates from co-pyrolysis and individual pyrolysis of PW and PC

Comparison of co-pyrolysis case with the calculated weighted average value from individual pyrolysis reveals a significant synergistic enhancement in H₂ and CO

while C_nH_m behavior was unchanged, see Fig. 64. This is mainly attributed to the interactions during co-pyrolysis of PW and PC yielding more oxygenated compounds and lowered hydrocarbons. In addition, cumulative CO_2 yield from co-pyrolysis was almost the same as that of weighted value.

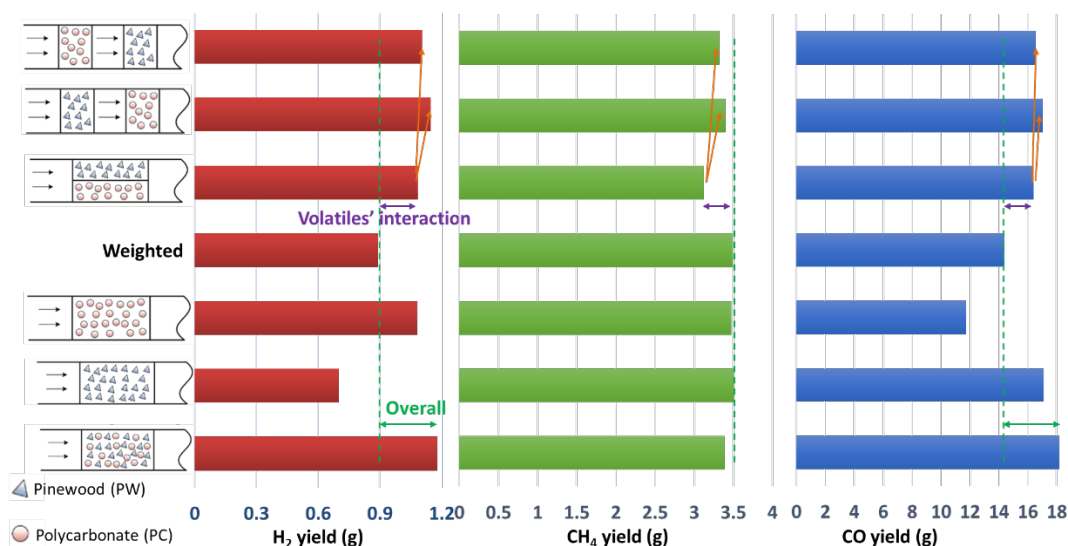


Figure 65. Cumulative yields of H_2 , CH_4 and CO from different feedstock arrangements to show the effect of volatiles in co-pyrolysis of PW and PC

Figure 65 shows that that volatiles mutual interactions were the primary contributor to H_2 , and CO yield enhancement while decreasing CH_4 yields. This is possibly from the mutual H and O transfer between PC and PW respectively. During the co-pyrolysis of PW and PC, the oxygen-containing radicals originating from PW decomposition were characterized with low stability, which helped to crack the phenolic intermediates evolved from PC degradation [175], resulting in reduced tar yield but enhanced H_2 and other gas components formation[176,177]. On the other hand, the H rich radicals originating from the fracturing of side chain in PC degradation acted as H-donor species to suppress the secondary condensation and repolymerization of evolved PW volatiles

[118], thereby reducing secondary tar formation and accordingly facilitating the conversion of gaseous products. This was similar to PW+PS case as reported earlier.

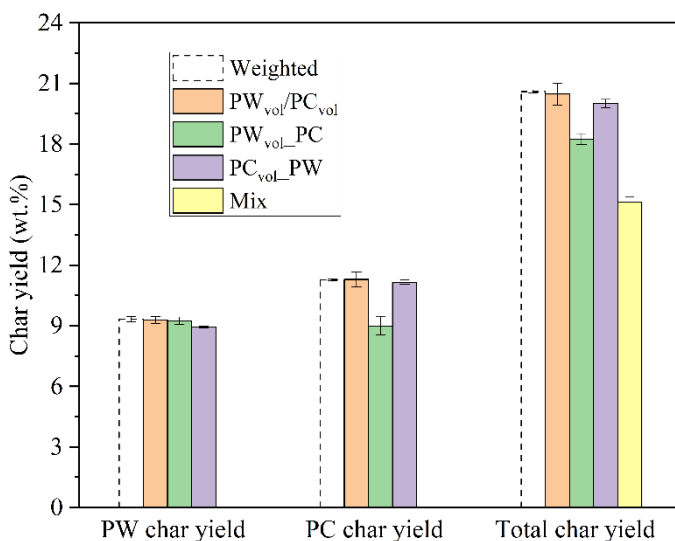


Figure 66. Char yield from co-pyrolysis of PW and PC with feedstock configurations of volatiles interaction

Figure 66 further shows that PW char yield in PW_{vol}_PC case was close to that of weighted value from individual pyrolysis, while PC char yield in PW_{vol}_PC case was significantly decreased. The enhancement in H₂ yield, better overlap in H₂ evolution, and significant reduction in PC char yield observed in PW_{vol}_PC case confirmed that the interactions between PW volatiles and PC melt contributed to the enhanced PC degradation. The underlying mechanism for this promoted PC degradation can be attributed to the abundant oxygenates radicals in PW volatiles with high reactivity, which attacked the PC chain causing enhanced depolymerization of original PC backbone and promoted chain scission of PC oligomers [152]. However, the cumulative H₂ yield in PC_{vol}_PW case only presented a slight increase as compared to PW_{vol}/PC_{vol} case, even though extra interactions between PC volatiles and solid PW

were involved when PW was placed downstream. This result indicates that the abundant phenolic intermediates in PC volatiles were relatively stable and thus did not effectively interact with decomposing PW. PW char yield in PC_{vol}_PW case only slightly decreased as compared to that of weighted value, see Fig. 66. This further confirms the stability of phenolic intermediates in evolved PC volatiles. The slight reduction in PW char yield observed in PC_{vol}_PW case may result from the suppressed cyclization and aromatization reactions in PW decomposition with the presence of H-donor radicals from PC volatiles.

From Fig. 65, that volatiles mutual interactions in PW_{vol}/PC_{vol} case favored CO formation while inhibiting CH₄. This can be explained from hydrocarbon radicals in PC volatiles interacted with oxygenates in PW volatiles to enhanced oxygenated compounds generation while suppressing light hydrocarbons formation. Oxygenated compounds underwent further decarbonylation and decarboxylation reactions to release CO and CO₂, which interpreted to promoted CO and CO₂ yields. This enhanced pathway for oxygenated compounds formation was confirmed in a recent study [148], in which the TG-FTIR analysis showed that the intensity of C=O bond from co-pyrolysis of lignin and PC was synergistically enhanced. Moreover, it is noteworthy that the CO and CH₄ yields of PW_{vol}_PC case were higher than that of PW_{vol}/PC_{vol} case, mainly because the additional interactions between PW volatiles and PC melt involved in PW_{vol}_PC case facilitated PC degradation and accordingly enhanced the conversion of PC feedstock to gaseous products.

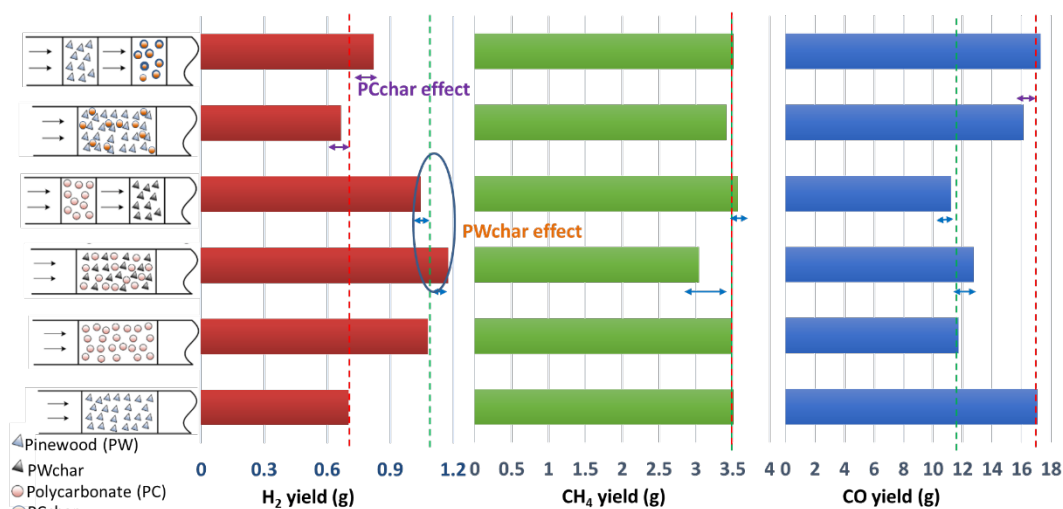


Figure 67. Cumulative yields of H₂, CH₄ and CO from different feedstock arrangements to show the effect of chars in co-pyrolysis of PW and PC

To understand the influence of chars from PW and PC on the co-pyrolysis behavior different feedstock configurations involving these chars were tested. Figure 67 shows the influence of these effects on H₂, CH₄ and CO yields. The interactions between PW char and PC melt were expected to be more pronounced than interactions between PC char of PW feedstock in co-pyrolysis of PW-PC mixture due to the better decomposition overlap. There results indicated that the addition of PW char significantly affected PC decomposition. The changes in gas yields presented here can be interpreted by the following pathways. As discussed above, PC pyrolysis yielded a wide range of phenolic intermediates with hydroxyl groups (C_{aromatic}-OH) and ester groups (C_{aromatic}-O-C) bonded to benzene ring. It is reported with the bond dissociation energies for these groups were in the order of C_{aromatic}O-C < C_{aromatic}-OC < C_{aromatic}-OH [178,179]. Hence, in pure PC pyrolysis, the cleavage of C_{aromatic}O-C bond with lower dissociation energy tended to occur, resulting in the release of aliphatic hydrocarbon side chains, and followed by cracking reactions to form light

hydrocarbons. While in the case of pyrolysis of PW+PC char mixture, PC degraded in the presence of abundant alkali and alkaline earth metals (AAEMs) from PW char. It is reported that AAEMs in biomass char and the porous carbon in the char had catalytic effect in deoxygenation of phenolic intermediates [180]. This enhanced the cleavage of $C_{\text{aromatic}}\text{--OC}$ and $C_{\text{aromatic}}\text{--OH}$ bonds to form more oxygen-containing groups, followed by decarbonylation and cracking reactions to yield more CO and H₂ at the expense of declined C_nH_m yield. Additionally, AAEMs and porous carbon in biomass char catalyzed the cracking of PC oligomers and primary pyrolysis products [181], contributing to enhanced H₂ formation. Wang et al. reported that the inherent AAEMs in biomass had detrimental effects on yields of both light hydrocarbons and aromatic hydrocarbons from pyrolysis [182]. With support from the literature, we can say that the AAEMs in biomass char showed great catalytic effect on PC degradation. The presence of AAEM in PW char also facilitated Boudouard reaction which was found to decreased CO₂ and char yields and enhance CO yields. The relatively lower surface area of PC char led to insufficient active sites to support the interactions between PC char and PW. Hence, a minimal effect of PC char on PW pyrolysis was exhibited here which led to increased H₂. We suggest further studies into the solid-solid interaction between biomass and plastics, especially PW-PC mixtures, to provide concrete understanding of the char effects in these cases and chemical reactions associated with feedstocks with overlapping pyrolysis temperatures.

Chapter 8: Conclusions and Future Work

8.1 Introduction

These novel results provided in the above chapter on into the sources of synergistic interaction and their contribution are essential to develop co-pyrolysis and co-gasification processes of biomass and plastic wastes. They not only provide the mixing strategies, compatibility, and optimal composition for these feedstocks but also helps to enhance synergistic routes for syngas production while minimizing the inhibitive interactions that have the tendency to either limit the syngas production or cause material handling difficulties that are particularly observed in separate processing of biomass and plastics.

8.2 Characteristics of interaction between biomass and hydrocarbon polymers

The synergistic interaction studies between biomass and synthetic polymer waste were classified based into different types of polymer composition. Investigation into biomass interaction with hydrocarbon polymers were carried out using pinewood as a biomass representative and polypropylene as the hydrocarbon polymer representative. Steam gasification of pinewood with polystyrene revealed significant synergistic enhancement of H_2 and CO_2 yield while decreasing low molecular mass hydrocarbons and CO yield and no significant synergy was observed in the net carbon conversion. This behavior was suggested to be from interaction during secondary reforming that lead to improved reforming of the volatiles to form H_2 . TGA investigation into these mixtures and subsequent kinetic modeling revealed that the

biomass and polypropylene decomposition peaks do not have significant overlap and their co-pyrolysis does not show any interaction of significance. Modeling results revealed broadening of the activation energy distribution of the biomass and that the interaction showcased in TGA environment was predominantly from physical nature of the polymer and its melt-phase causing diffusion limitations in the biomass devolatilization. It revealed that 25% polypropylene content in the biomass resulted in maximum interaction. In addition, a synergistic reduction in the char yield was also observed from the TGA examination to suggest an enhanced devolatilization from the solid-biomass followed by their delayed evolution through the melt-phase.

To further our understanding of the source of interactions and their respective contributions to the syngas evolution, deconvoluted feedstock arrangements were studied in the lab-scale semi-batch reactor. Comparisons between co-pyrolysis of pinewood-polypropylene mixture and individual components pyrolysis revealed significant enhancement of syngas production. Total syngas yield, H₂ yield and CO yield with co-pyrolysis were enhanced by 27%, 80% and 63%, respectively, as compared to the weighted aggregates from individual pyrolysis while char residue also decreased. However, no apparent synergistic enhancement was observed in the C₁ and C₂ hydrocarbon yield. The cumulative analysis indicated a delayed syngas evolution in co-pyrolysis, mainly from the result of delayed C₁ and C₂ release.

Separated feedstock configurations showed that the mutual volatile interaction led to reduced hydrocarbon formation while significantly enhancing H₂ and CO yield. Oxygenated radicals in pinewood volatiles and hydrocarbon radicals in polypropylene volatiles interacted to yield more oxygenated compounds and lowered hydrocarbons.

Moreover, the hydrogen rich radicals from polypropylene degradation acted as H-donor species, which enhanced the pinewood devolatilization and suppressed the condensation and repolymerization reactions with reduced tar and char formation. The cumulative analysis revealed that the mutual interactions between the volatiles accelerated the evolution of each gas component during co-pyrolysis.

Co-pyrolysis of pinewood char and polypropylene with evenly mixed and separated configurations indicated that the catalyst effect of pinewood char was negligible with evenly mixed configuration but profound when the polypropylene and pinewood char were separated. With the coexistence of polypropylene and pinewood char, the porous structure of pinewood char was easily blocked by the polypropylene melt, which hindered the contact of pinewood char with evolved polypropylene volatiles. Moreover, the polypropylene melt existed in char holes pyrolyzed slowly due to the poor heat conductivity, which was responsible for the delayed hydrocarbon and syngas evolution in co-pyrolysis of pinewood-polypropylene mixture

8.3 Characteristics of interaction between biomass and aromatic polymers

Further investigations were carried out with similar biomass feedstocks and different aromatic polymer wastes. These investigations included pinewood, paper waste and pine bark as the biomass and polystyrene and waste tires as the aromatic polymers [183]. Here aromatic polymer refers to a monomer composition with at least one aromatic ring and almost no hetero-atoms (O or Cl etc.). Co-pyrolysis and CO₂-assisted-co-gasification environments were utilized to understand these interactions between pinewood and polystyrene, and pine-bark and waste-tires.

The pine-bark and waste-tire blends provided no interaction and thus their syngas behavior was a weighted aggregate of the individual feedstock behavior. But co-pyrolysis was found to provide inhibitive behavior in terms of decreasing the BET surface area of the chars obtained which was consistent even in TGA studies to suggest the relatively higher stability of the char present in waste-tires. This is from the high stability and low surface area of carbon black added to waste-tires for reinforcement. Additionally, the volatiles from the waste-tire also showed no impactful interaction with the biomass volatiles. This also suggests their stability to the oxygenated radicals from the biomass. While the lack of any inhibitive behavior in these studies suggests the feasibility of pyrolysis and gasification to convert waste-tires with biomass, the high char yield, and its relative resistance to react with CO₂ to gasify into syngas means that appropriate pathways of value need to be developed for the char yield from this process. High-value carbon products such as carbon nano-tubes, quantum dots, activated carbon and carbon black recycling can be the potential pathways, but further research is necessary to understand the viability of this approach.

In the case of polystyrene, its interaction with paper waste was initially investigated in pyrolysis and CO₂-gasification environments as polystyrene is commonly encountered in landfilled destined wastes and is often spoiled with food/paper waste. TGA studies showed that the polystyrene had no influence on the decomposition behavior of paper waste while the char formed from paper delayed the polystyrene decomposition possibly by forming more stable compounds. Product gas analysis of paper-polystyrene during co-pyrolysis and CO₂ co-gasification in a semi-batch reactor revealed that co-processing yields more gaseous products than the

weighted aggregate of conversion of individual components (paper and polystyrene). For plastic content of 10–30%, the H_2 , CO , CO_2 , product gas and energy yield provided the highest synergy during co-pyrolysis. This is because volatiles from the paper decomposition enhanced the decomposition of polystyrene and slowed the reaction rate to lower the char yield contribution from polystyrene when pyrolyzed with paper. However, when these mixtures were co-gasified for different feedstock mixture values, the CO yields were lower compared to mono-gasification. The char-forming tendency lowered in polystyrene with the presence of paper. The volatiles caused lower amounts of char left for CO_2 to react via Boudouard reaction to form CO . This caused an increase in CO_2 evolved (mostly unreacted) during CO_2 co-gasification compared to mono-gasification. For plastic content of 20%, the energy yield, and product gas yield were highest for both co-pyrolysis and co-gasification compared to other feedstock compositions because this results in high char yields from the paper which increased the decomposition rate of polystyrene to increase in the product gas yield and energy efficiency. These results not only provide the quantified impact of this interactive behavior, but also an insight into the importance of conditions necessary for char formation and its conversion to effectively improve syngas formation. So, upscaling of gasification of these mixtures need to consider the impact of operating conditions on the char formation and choose the residence times to optimize the syngas yield.

To isolate and quantify the interactions observed between polystyrene and biomass, co-pyrolysis of polystyrene with pinewood was investigated using a series of feedstock arrangements as mentioned in the respective chapters. Co-pyrolysis of pinewood (PW) with polystyrene (PS) in a lab-scale semi-batch reactor was found to

synergistically enhance the yield of syngas components such as H_2 , and CO by 80% and 67% respectively compared to weighted yields from individual pyrolysis. The interaction can be split into interaction between different intermediate groups from the biomass and polystyrene such as volatiles, char, and unreacted-feedstock/feedstock-melt. These studies using different configurations revealed that, PS-volatiles are catalytically cracked over PW-char to increase H_2 yield by 63%, and CH_4 by 18%, only when the PS-melt is not in contact with PW-char. PS-melt tends to cover the PW-char's active sites to avoid any catalysis. The secondary reactions between PS-volatiles and PW-volatiles were found to be a major contributor to the synergistic interaction observed in co-pyrolysis. This interaction improved mutual H-transfer from PS-volatiles and O-transfer from PW-volatiles to enhance the reforming of the volatiles and result in improved kinetics to result in increased yield of H_2 by 40% and CO by 46%, while mildly decreasing CH_4 and C_2 yields. The interactions of PS-volatiles with unreacted-PW, and PW-volatiles with PS-melt were both found to be detrimental to the syngas components' yield, to result in decreased CH_4 and CO yields in both cases and decrease in H_2 yield in the latter case. Some limitations were observed in deconvoluting the interaction between PS-volatiles+unreacted-PW from PS-volatiles interaction with complete-feedstock, especially with respect to H_2 behavior. The interaction between PS-melt and unreacted PW was found to be inhibitive in terms of kinetics, while segregating its influence on the yield of syngas was found to be difficult due to the limitation of separately capturing PS-volatiles+unreacted-PW. In conclusion, volatile-volatile interactions, and biochar catalysis were the main positive contributors to

synergy in syngas yields while volatile-feedstock and solid-phase interactions were impeding their co-pyrolysis.

8.4 Characteristics of interaction between biomass and oxygenated aromatic polymers

Here oxygenated aromatic polymer waste refers to polymers with a monomer composition of at least one aromatic ring and C-O bond. For these, we utilized pinewood as the biomass and polyethylene terephthalate and polycarbonate as the oxygenated aromatic polymer wastes. Polyethylene terephthalate has one aromatic ring with two ester groups per monomer while polycarbonate has two aromatic rings and a single ester group per monomer. Both these were initially investigated in steam gasification environment followed by deconvoluted co-pyrolysis tests using only polycarbonate.

Steam co-gasification of polyethylene terephthalate and polycarbonate with pinewood revealed synergistic enhancement of H_2 , and CO_2 while decreasing CO relative to CO_2 . The hydrocarbon yield was additive and showed no synergy and carbon conversion showed only a mild increase in the case of polyethylene terephthalate. In the case of polycarbonate, carbon conversion improved significantly and the synergy in the hydrocarbon yield was dependent on the feedstock composition. This suggested the presence of volatile interactions and its impact in improving cracking, and reforming to form increased H_2 . The methyl groups in polycarbonate also interacted with the oxygenates from biomass to modify the hydrocarbon yield while the lack of such groups in polyethylene terephthalate led to the indifference. The ester groups interacting with the oxygenate radicals from biomass also led to improved CO_2 yield

and its selectivity compared to CO. The presence of aromatic radicals was suggested to be a contributor to improved carbon conversion, possibly from solid-phase interaction.

To further examine this interaction, TGA was utilized along with kinetic modeling. TGA revealed an interaction between this type of plastic wastes and biomass. The extent of synergy between biomass and plastics directly scaled with the amount of benzyl groups in them. Additionally, the reason for this interaction could be from the oxygenated groups in both these feedstocks reacting with the active sites on the biochar. The char yield was also found to synergistically decrease in both these cases. Broadening of activation energy distribution was also observed in the case of polyethylene terephthalate while additional activation energy peaks were also observed to suggest the diffusion limitation from the melt-phase along with added interactive reactions.

In the case of biomass with polycarbonate, the change in activation energy distribution plot was completely different compared to the previously ones. The low activation energy peaks from polycarbonate became narrow and merged with the pinewood decomposition peak. The reason for such behavior can be seen in the significant overlap between the pyrolysis temperature of polycarbonate and pinewood. This overlap also led to non-additive mass-loss behavior which increased the low-temperature peak and decreased the high temperature peak. It showed that the interaction between the solid-phases is also present in biomass-plastic wastes in certain feedstocks.

To delineate the co-pyrolysis of pinewood with polycarbonate, the tailored feedstock arrangements were utilized in the lab-scale fixed bed reactor. The yields of

H₂, CO, and total syngas from co-pyrolysis were enhanced by 33%, 26%, and 19%, respectively, as compared to the weighted average values from pyrolysis of individual components, while char and tar yields remarkably decreased. Separated feedstock studies revealed that the volatiles interaction led to increased H₂, CO, and CO₂ while suppressing hydrocarbon yield. This is mainly from the interaction between the hydrocarbon radicals of polycarbonate with the oxygenates from biomass. The oxygenate radicals from pinewood were able to improve the decomposition of polycarbonate while the vice-versa showed no promotion, due to the relatively higher stability of polycarbonate volatiles and their delayed evolution compared to pinewood decomposition. The results also showed that volatiles interaction preferred to increase syngas while the solid-phase interaction delayed syngas evolution due to the unreacted polycarbonate behavior.

The pinewood char was also found to enhance the decomposition of polycarbonate even when in direct contact while the vice-versa also showed no impactful interaction. This catalysis in the presence of direct contact contrasts with our results from polypropylene and polystyrene where direct contact inhibited such catalysis while maintaining a separation resulted in catalytic improvement. This shows that polycarbonate melt-phase can decompose on the biomass and its tendency to char results in an escape for the volatiles and thus allowing for the catalysis to occur while the other plastics only devolatilized and never charred. This resulted in barrier being sustained in the cases of polystyrene and polypropylene.

8.5 Recommendations for Future Work

These results on co-processing of biomass with synthetic polymer waste shows remarkable synergistic improvements in the process performance and further development is necessary in this regard. The future investigations in this regard need to focus on validating these modeled interaction behavior results using a continuous gasifier to understand the relative importance of interaction between different groups and their quantified effects on the reliable and consistent operation of such process. While molecular scale synergistic interaction studies can be pursued as started recently in the literature [169], due to the diversity in solid wastes that are available for energy extraction and its tendency to be contaminated, the focus needs to be on the versatility of the process and not the specificity of the feedstock. A comprehensive tabulation of interaction between different classes of polymer wastes and biomass can be built in the future, starting with the results in this dissertation. This tabulation will provide the tendency of the interactions and their impact on different products including syngas and char.

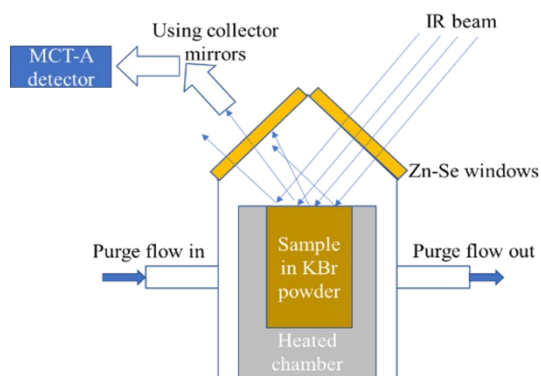


Figure 68. A schematic of in-situ diffuse reflectance FTIR for solid-phase interaction studies

Micro-scale investigations will need to be based on classes of feedstocks and not specific feedstock. Novel techniques such as in-situ diffuse reflectance infrared spectroscopy as shown in Fig. 68 can be utilized to understand the intricate solid-phase interactions that are possible between biomass and synthetic polymer wastes [184]. Py-GC/MS-TCD studies also need to be expanded to observe the influence of co-processing on the volatile intermediates. These results can add further details to the synergy model developed in this work to improve its applicability to different feedstock classes and operating conditions.

While syngas is the main product from co-gasification, due to the restriction on the residence times that are scalable, char formation is inevitable. Additionally, the value of gasification is low when the syngas is only used for energy purposes. To improve the viability of such operation, the char collected from the process needs to be processed into carbon products with high economic value. Developing an efficient pathway to convert this char yield into products such as graphene, quantum dots, activated carbon, and metal/C catalysts can improve the process viability by diversifying the applications to include petrochemical, biomedical, chemical, and pharmaceutical industries. The high-value of these carbon products can compensate the economic variables in gasification process.

Gasification is limited in its viability to biomass with relatively low moisture content. But significant solid wastes such as wastewater sludge, yard waste, food waste, wet manure wastes and other low-grade biowastes are disposed in significant quantities with resource consumption. A viable and self-sufficient pathway to dispose these types of wet-wastes is necessary. Supercritical CO₂ assisted carbonization of these wastes

can potentially convert them into high-density carbon products while the supercritical CO₂ can provide efficient dewatering and product extraction. Using appropriately scalable reagents, high-value carbon products can be produced from these wastes which can result in an economically advantageous disposal of these wastes. Preliminary results using cellulose provided promising carbon micro-spherical clusters formed via this process. Further proof-of-concept and expansion of this route can have significant traction in the production of value-added products from wastes.

List of Published Papers and Book Chapters

This dissertation was recreated from the research articles produced by the author along with collaboration in the Combustion Lab, UMD. Appropriate permission was taken from lead co-authors in necessary cases to ensure integrity in this dissemination. Given below is the list of articles published/under-review during this work.

Book Chapters:

- [1] Burra KG, Gupta AK. Thermochemical Reforming of Wastes to Renewable Fuels. In: Runchal AK, Gupta AK, Kushari A, De A, Aggarwal SK, editors. Energy Propuls. A Sustain. Technol. Approach, Singapore: Springer Singapore; 2018, p. 395–428. doi:10.1007/978-981-10-7473-8_17.
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Journal Papers:

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