# RECENT DEVELOPMENT OF BIOMASS AND PLASTIC CO-PYROLYSIS FOR SYNGAS PRODUCTION

## ABSTRACT

Co-pyrolysis is an enhanced thermochemical conversion process employed to convert lignocellulosic and plastic materials into more improved liquid, gaseous, and solid biofuels. Co-pyrolysis has been used extensively for the manufacturing of liquid biofuels (bio-oil) with little emphasis on syngas production. However, syngas is a promising source of renewable power generation and green chemicals. Production of syngas provides an opportunity for achieving negative $CO_2$ through the implementation of carbon capture and storage. This paper reviews the production of syngas through co-pyrolysis of plastic and biomass wastes in a typical municipal solid waste from Ghana. The effects of key production parameters including type of feedstock, temperature, catalysts, heating rate, reactor configuration, and residence time on the yield and composition of the syngas are outlined. The paper attempts to unravel the kinetic mechanisms of the co-pyrolysis process and the synergistic effects that co-exist between the feedstocks during syngas production. It was found that syngas can be optimized in terms of yield and quality to be used as transportation fuels, chemicals, and the production of electricity through the co-pyrolysis process.

# 1. INTRODUCTION

The focus of scientists and engineers worldwide has turned to the usage of renewable and sustainable sources of energy including biomass to supplement and eventually replace conventional energy resources such as coal, crude oil, and petroleum in the long term [1]. The search for sustainable alternatives to fossil fuels is particularly relevant in recent times due to the rise in global energy demand, prize hikes, predictions of extinction, and climate change. Zhang et al. [2] and Khan et al. [3] postulated that biomass and plastic usage in the production of fuels can ensure energy security and waste treatment.

In Ghana, the analysis of municipal solid waste (MSW) composition was 61 % organics, 14 % plastics, 6 % inert, 5 % miscellaneous, 5 % paper, 3 % metals, 3 % glass, 1 % leather and rubber, and 1 % textiles. MSW is composed of varied materials; however, biomass and plastics make up the greater part, which can successfully be used to produce syngas [4,5]. Biomass (wood, agricultural, and forestry residues) has been acknowledged as a major renewable reserve for biofuel production, and it is anticipated that biomass energy would continue to play a crucial role in minimizing climate change and global warming [6]. Kim et al. [7] reported that an increase of 1 % per capita biomass fuel use reduces $CO_2$ emissions by 0.65 % per capita. This claim is supported by the works of Sulaiman et al. [8] who found that the amount of $CO_2$ could be reduced by up to 0.8888 % in twenty-seven European Union (EU) countries by an increment of 1 % of wood biomass utilization. The availability of biomass is unquestionable. The global production is approximately 220 billion tons annually [9] with Ghana contributing about 97,000 metric tons annually from agroforestry waste [10]. Unlike biomass, plastics are non-biodegradable and cause environmental pollution when disposed of improperly. Eleven (11) million tons of MSW with about 10-14 % plastic composition is generated in Ghana annually [11,12]. Plastic wastes comprise hydrocarbons as their major composition since they are produced from petroleum products [13]. Due to its rich content of hydrogen resources, co-pyrolyzing with lignocellulosic biomass enhances the carbon and hydrogen contents in the feedstocks, thereby improving the quality and yield of the bio-oil [14–16], char [17,18], and syngas [19,20] during co-pyrolysis and co-gasification.

Co-pyrolysis is a thermochemical approach similar in operation to mono-pyrolysis but utilizes multiple feedstocks to obtain products of high yield and quality when compared to its separate results. Chin et al. [21] found that co-pyrolysis of biomass and plastics is a promising method to produce syngas from MSW as compared to conventional methods such as landfilling and incineration. Co-pyrolysis as technology has gained prominence because of its simplicity and success in enhancing the production of especially the bio-oil in addition to syngas and char. Having said that co-pyrolysis can also be employed in optimizing the yields and compositions of any of the three products (liquid, gas, char) by adjusting the operating conditions [9]. For instance, syngas is optimized with conditions of high temperatures, low heating rates, longer residence times, and the addition of catalysts [22,23]. Syngas is produced mainly through pyrolysis and gasification [24]. Trabelsi et al. [25] observed that the calorific value of syngas produced from pyrolysis of Tunisian solar-dried sewage was 9.96 MJ/m$^3$ whereas the calorific value of syngas from gasification of the same feedstock was found to be 8.02 MJ/m$^3$. The result was attributed to the high contents of hydrogen ($H_2$) and methane ($CH_4$) present in the pyrolysis syngas. Déparrois et al. [19] researched on the production of syngas from co-pyrolysis and co-gasification using $CO_2$ as the gasification/gasifying agent. They observed that the co-pyrolysis syngas had increasing hydrogen content as well as yields. It is worth noting that raw syngas is composed of both wanted (CO, $H_2$, $CO_2$, and $CH_4$) and unwanted substances ($H_2S$, $CS_2$, HCl, HF, Na, K,) that need to be cleaned before they can be used for downstream purposes [26] and fractions of the composition are dependent on several indicators including the type of feedstock, production conditions, and intended use of the syngas. On one hand, Lee et al. [27] found that pyrolysis syngas requires no additional upgrading methods compared to bio-oil and char and can be used to directly fuel gas turbines, gas engines, boilers, etc. for power production,

among others. Also, Bellouard et al. [28] observed that syngas generated through pyrolysis using concentrated solar energy as a heat source incurs no extra expenses on upgrading methods. On the other hand, several researchers including Abdoulmoumine et al. [26], Shen et al. [29], Roddy [30], Policella et al. [31], Sansaniwal et al. [32], and Woolcock and Brown [33] have contrasting views which are discussed further below.

This paper reviews the mechanism of biomass and plastic waste co-pyrolysis to produce syngas from a typical MSW in Ghana. The key operating parameters affecting syngas yield and quality, including types of feedstocks, reactor configuration, temperature, heating rate, residence time, and the use of catalyst have been discussed. The paper explores the various applications of syngas and possible upgrading methods to improve syngas quality.
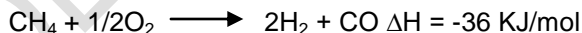

## 2. SYNGAS

Syngas or synthesis/synthetic gas is a form of industrial gas fuel with hydrogen ($H_2$) and carbon monoxide (CO) as its main composition [24,30,33]. Syngas is a term usually used as an industry shorthand to refer to the product gas from all kinds of gasification processes [33,34]. It is noteworthy that syngas is also one of the three substantial intermediate products of pyrolysis of MSW. For this review, syngas will be used, however, numerous other terminologies can be found in literature including;

- Producer gas [35]
- Non-condensable gas [36]
- Pyrolytic gas [37]
- Bio-syngas [27]
- By-product/surplus gas [38]

## 2.1. SYNGAS PRODUCTION METHODS

Syngas can be produced from any carbonaceous material (biomass, polymers, coal, natural gas, etc.) through technologies like pyrolysis, gasification, combustion, partial oxidation, hydrogenation, and steam reforming [24,39,40]. Although combustion produces some form of gases, it is not considered a favorable syngas production method. This is because the gases produced do not have any significant heating value, among others [39–41]. Partial oxidation is an exothermic reaction that produces syngas from a non-catalytic reaction of methane and oxygen [39,42]:

$$CH_4 + 1/2O_2 \longrightarrow 2H_2 + CO \quad \Delta H = -36 \text{ KJ/mol}$$

Al-asadi et al. [43] found that waste plastics can be used to produce syngas through partial oxidation by the addition of catalysts by a modern technology known as catalytic partial oxidation. A detailed review of catalytic partial oxidation of natural gas and renewable hydrocarbons for syngas production can be found elsewhere [42]. According to Leonzio [44], syngas can be produced through the hydrogenation of carbon dioxide. The syngas produced via this technique has a higher hydrogen-to-carbon (H/C) ratio [39]. Steam reforming is probably the oldest of all the syngas production methods which began as early as 1926. Unlike partial oxidation, steam reforming is an endothermic reaction that produces syngas from the catalytic reaction of methane and steam [39,42,45]:

$$CH_4 + H_2O \text{ (catalyst)} \longrightarrow 3H_2 + CO \quad \Delta H = +206.2 \text{ KJ/mol}$$
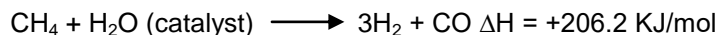
Compared to the partial oxidation method, steam reforming produces syngas with a much higher hydrogen-to-carbon monoxide ($H_2$/CO) ratio [46]. All the methods discussed so far

are best used when converting natural gas (methane) into syngas. However, the main waste-to-energy technology for producing syngas from MSW especially, biomass and plastics are pyrolysis and gasification [31]. These two thermochemical processes have been used most compared to other conversion processes because of their feedstock flexibility, high throughput, and efficacy, among others (19). In pyrolysis, solid carbonaceous feedstocks are converted into syngas, bio-oil, and char in an inert atmosphere [47] whereas gasification transforms solid, liquid, and even gaseous feedstocks into syngas with tar and char as by-products [19,39]. The similarities and differences between the two technologies have been highlighted by several researchers. For example, Trabelsi et al. [25] reported that the presence of gasifying agents like steam, oxygen/air, $H_2O$, and $CO_2$ in gasification distinguishes it from pyrolysis. Also, production conditions including reactor temperature, gasifying agent, equivalence ratio (air or oxygen), feedstock composition, and pressure, among others affect the quantity and composition of syngas from both technologies [19,25]. One distinguishing factor between pyrolysis and gasification is the temperature range. Pyrolysis starts with a much lower temperature range compared to gasification. For instance, temperature ranges of 300 – 900 °C [25], 300 – 1300 °C [48], and 650 – 1200 °C [49] have been reported for pyrolysis. For gasification, temperature ranges of 790 – 1650 °C [49], 800 – 1200 °C [48], and 750 – 800 °C [50] have also been reported.

According to Moghadam et al. [51], pyro-gasification (i.e. the combination of pyrolysis and gasification) improves the syngas yield and quantity in terms of the heating value, low tar content, among others. An excellent review by Block et al. [52] has discussed in detail the co-pyrogasification of biomass and plastics to obtain high-grade syngas fuel. Zhang et al. [2] studied high-quality production of hydrogen-rich syngas from pyrolysis-gasification of biomass and plastic wastes using Ni-Fe@Nanofibers/Porous carbon catalyst and observed that a two-stage pyrolysis-gasification system improves the syngas quality by increasing the $H_2$ content when compared to single-stage pyrolysis or gasification approach.

## 2.2. SYNGAS CHEMICAL COMPOSITION

Raw syngas normally called producer gas consists of several useful organic and inorganic compounds such as methane ($CH_4$), carbon monoxide (CO), carbon dioxide ($CO_2$), hydrogen ($H_2$), ammonia ($NH_3$), hydrochloric acid (HCl), benzene ($C_6H_6$), toluene ($C_7H_8$), hydrogen sulfide ($H_2S$), among others depending on the feedstock. Nonetheless, researchers agree that the main chemical compositions of syngas are $H_2$ and CO [24,26,30,33,53]. Mohan et al. [54] found that the core compositions of syngas from the pyrolysis of wood/biomass are CO, $CO_2$, $H_2$, $CH_4$, $C_2H_4$, $C_3H_6$, and traces of other hydrocarbons. Williams and Williams [55] averred that the cardinal constituents of syngas from pyrolysis of plastics are $H_2$, $CH_4$, CO, $CO_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, $C_3H_8$, $C_4H_8$, $C_4H_{10}$, and HCl. Similarly, the constituents of syngas from the co-pyrolysis of pine biomass and a mixture of PE, PP, and PS plastic wastes were investigated using gas chromatography (GC) by Paradela et al. [56] and categorized under alkanes, alkenes, CO, and $CO_2$. Jun et al. [57] studied hydrogen-rich syngas produced from the co-pyrolysis of MSW and wheat straw at a temperature range of 500 - 1000 °C in a drop-tube furnace. They found $H_2$, CO, $CH_4$, $CO_2$, $C_2H_4$, $C_2H_6$, and $C_xH_y$ as the syngas' main constituents. It should be noted that there are traces of impurities that also needs to be considered before using the syngas. These contaminants include dust, tars, alkali metals such as K and Na, BTX (benzene, toluene, xylenes), sulfur-, nitrogen-, and chlorine compounds (e.g. $H_2S$, COS, $NH_3$, HCN, HCl), and heavy metals (e.g. Hg, Cd) [58].

## 2.3. OPTIMUM CONDITIONS FOR SYNGAS PRODUCTION

Even though syngas can be used as a chemical feedstock for the manufacture of ammonia, hydrogen, and other valuable products, Soria et al. [59] observed that improving the quality

of syngas and maximizing its yield is tantamount to the promotion of the efficient and successful conversion of biomass materials for the manufacture of these valuable products. The yield and quality of syngas can be optimized by carefully selecting and fine-tuning the feedstocks and operating conditions, respectively. According to Dewangan et al. [22] and He et al. [23], syngas quality and yield can be optimized by the preferred conditions of high temperatures, low heating rates, longer residence times, and the use of catalysts. Wang et al. [60] studied hydrogen-rich syngas production from catalytic co-pyrolysis of polyvinyl chloride (PVC) and waste paper (WP) blends. They reported that the highest $H_2$ yield (429 $\mu mol^{-1}.g_{cat}^{-1} min^{-1}$) was recorded at a temperature of 900 °C with a mixing weight ratio of 60 %PVC and 40 %WP. Furthermore, the addition of $CeO_2$-CaO and RuZSM-5-CaO catalysts greatly promoted $H_2$ production. Wu et al. [61] performed co-pyrolysis of lignocellulosic biomass with low-quality coal: optimal design and synergistic effect from gaseous product distribution. Results showed that at a temperature of 600 °C, there was a significant improvement in the syngas yield from the co-pyrolysis of both wheat straw and three model compounds of lignocellulosic compounds (cellulose, hemicellulose, and lignin). The effects of operating parameters and moisture content on MSW pyrolysis and gasification were studied by Dong et al. [62]. The optimal operating conditions for syngas production with an energy conversion efficiency of 68.5 % were recorded at a temperature of 650 °C and an equivalence ratio of 4.0.

## 2.4. SYNGAS INDUSTRIAL APPLICATIONS

Syngas is a very useful commodity with its application in power and/or heat production (electricity generation, direct firing in boilers); commodity chemicals (ammonia, carbon dioxide, methanol); and transportation fuels (biodiesel, biogas, hydrogen). Figure 1 depicts the conversion technologies leading to the conversion of syngas into a host of chemicals. From the Figure, it can be seen that syngas can be converted into ammonia, methanol, waxes diesel, and olefins gasoline via the Fischer-Tropsch process, and many other useful chemicals. Furthermore, Methanol can be used for the production of several industrial chemicals including acetic acid, formaldehyde, methyl tertiary-butyl ether (MTBE), dimethyl ether (DME), etc. The production steps for each product can be found in the literature [30,63].
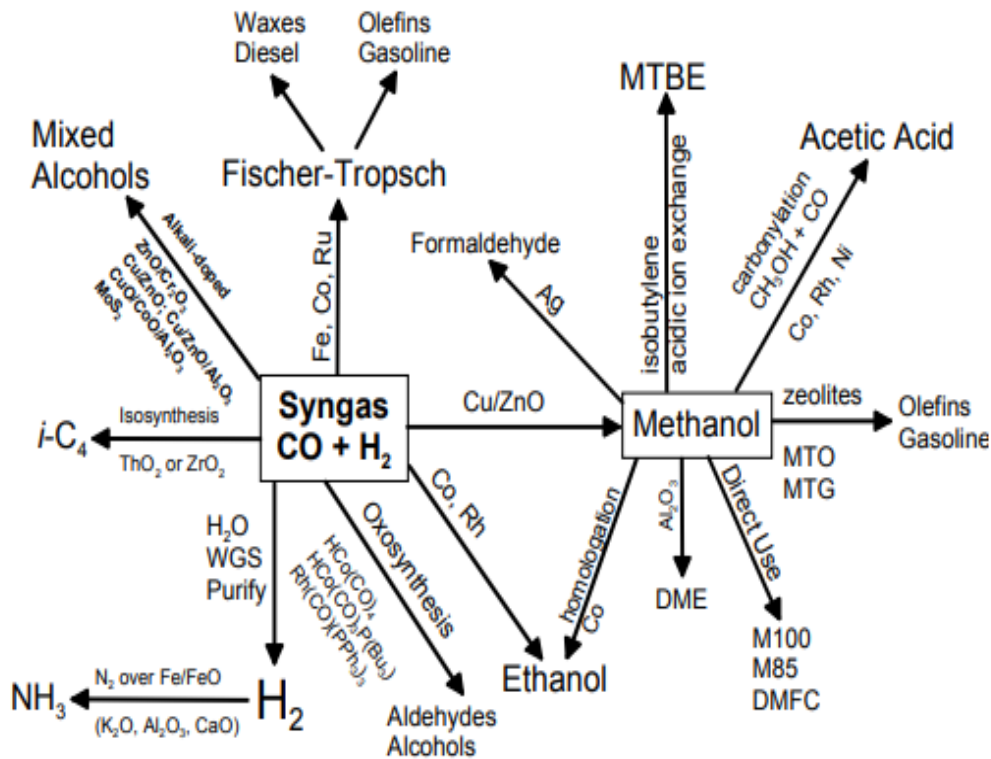
Figure 1: Syngas conversion technologies. Adapted from Woolcock and Brown [33]

## 2.5. SYNGAS UPGRADING METHODS

As mentioned earlier, raw syngas constitutes both essential and nonessential but valuable substances known as contaminants. These contaminants in the form of tars, particulate matter, nitrogen-containing compounds ($NH_3$, $NO_2$, etc.), sulfur-containing compounds ($H_2S$, $CS_2$, etc.), hydrogen halides (HCl, HF, etc.), and trace metals (Na, K, etc.) have deleterious effects on the process performance and equipment lifespan if left untreated [26]. Roddy [30] observed that syngas contaminants regardless of the concentration levels can cause severe technical and operational challenges. For instance, he mentioned that the tars can lead to catalyst carbonization and fouling, particulates can also lead to erosion, fouling, and plugging, among others.

Interestingly, few researchers averred in their works that syngas requires no additional upgrading methods. For example, Lee et al. [27] posited that the syngas upgrading process can be eliminated compared to bio-oil and char. As a result, it can be utilized to directly fuel existing boilers, gas turbines, and gas engines without any modifications. According to Bellouard et al. [28], syngas produced from wood biomass gasification with concentrated solar energy as the heat source require no further treatment. But Woolcock and Brown [33] and Shen et al. [29] opined that syngas should be treated for contaminants to ensure it meets the stringent environmental regulations before widespread usage. According to Policella et al. [31], syngas can only be used for power production using gas turbines and engines after the contaminants have been removed. Also, according to Sansaniwal et al. [32], syngas cannot be directly fed into gas turbines and engines for power production because of the negative side effects including cylinder corrosion, and piston choking, among

others. However, they observed that for boilers, the syngas can directly be applied for power production without necessarily treating the gas. These statements are in contrast with the statement made by Lee et al. [27]. The side effects of using untreated and treated syngas for power production can be considered for future research. It is noteworthy that several technologies exist for the cleaning of raw syngas. Notably, primary/in-situ and secondary methods are the two main approaches employed in syngas cleaning/upgrading. To distinguish between the two: primary/in-situ methods are the inherent approaches adopted to remove contaminants from the syngas during production while secondary methods are employed after the syngas is produced [29]. Secondary methods could further be divided into physical and chemical treatments. Besides these two cleaning technologies, an emerging technology known as a catalytic conversion, which engages the use of catalysts such as dolomite, zeolite, olivine, etc. can also be employed to purify raw syngas for downstream applications [32].

## 3. KEY SYNGAS PROCESS PARAMETERS

The end product of thermochemical processes such as co-pyrolysis is dependent on the careful selection of the process parameters. As a result, several studies have explored the best conditions for maximizing the yield and quality of syngas. Henceforth, it is imperative to unravel our understanding of the subject to achieve the desired result. In this section, the influence of key process parameters of co-pyrolysis syngas including temperature, heating rate, residence time, the addition of catalysts, feedstock type, and reactor type are discussed based on research findings.

## 3.1. TEMPERATURE

In the course of co-pyrolysis, the feedstocks are heated to an optimum temperature until the process is complete. The high operating temperatures of the co-pyrolysis process affect both the composition and yield of syngas, positively [32]. According to He et al. [23], the pyrolysis process is an endothermic system enhanced by increasing temperature. Sharypov et al. [64] investigated the role temperature has on pyrolysis product distribution using mixtures of beech wood and atactic polypropylene (1:1 weight ratio) in the temperature range of 350 – 450 °C. They found an appreciable increase in the gas fraction as the temperature increased. Yang et al. [65] studied syngas production through pyrolysis of biomass using Fe/CaO catalysts and the effect of operating variables on the process. It was found that both syngas yield and $H_2$ contents were improved significantly at higher temperatures. This finding is in broad concordance with a study performed by He et al. [23], who also reported that increasing temperature increases syngas production with a significant increase in $H_2$ and CO contents. Similarly, Dewangan et al. [22] studied the influence of temperature on co-pyrolysis of sugarcane bagasse and low-density polyethylene (LDPE). They reported an exponential increase in gas yield with an increase in temperature from 350 – 500 °C. Moghadam et al. [51] examined the optimum conditions of syngas production via biomass conversion through pyrolysis and air-steam gasification processes. They reported a maximum volume of 33.12 % for syngas in the pyrolysis zone at a temperature of 650 °C. The result of temperature on the upsurge of syngas volume was due to secondary cracking, reaction rate acceleration, and reforming reactions of heavy hydrocarbons according to Yang et al. [65] and Sharypov et al. [64].

## 3.2. HEATING RATE

Heating rate is a thermodynamic property and is defined as the rate of increase of temperature per unit of time [66]. Like pyrolysis temperature, the rate at which biomass samples are heated defines the outcome of the final product [63]. Aboulkas et al. [67]

examined the impacts of co-pyrolysis operating parameters on the final products of oil shale and plastics. They found that the conversion level and yield of syngas increased linearly with increasing heating rates from 2 – 20 °C/min at a set temperature of 500 °C. Efika et al. [68] studied the effects of temperature and heating rates – slow and rapid heating rates – on the pyrolysis products of refuse-derived fuel (RDF). The effects of heating rates (5, 20, 90, and 350 °C/min) on syngas yield and composition were evaluated and they found that the syngas yield increased from 14.4 – 46.9 wt.% whereas the oil yield decreased from 55 – 23 wt.% with increasing heating rates. Also, there was an observed increase in the syngas composition as the heating rate increased. A similar study was conducted by Safdari et al. [69] on the effects pyrolysis heating rate and temperature have on wildland fuels. Two different heating rates and temperatures were studied. The slow pyrolysis was done at a heating rate of 0.5 °C/s and a temperature of 500 °C whereas the fast pyrolysis experiment was done at a heating rate of 180 °C/s and temperature of 765 °C. They reported a higher syngas yield, tar yield, and volatile yield at the higher heating rate. Cahyono and Styana [70] studied the influence of temperature and heating rate on the pyrolysis of waste plastic bags. The experiment was performed in a fixed bed reactor using temperature ranges of 250 – 450 °C and heating rate ranges of 5 – 15 °C/min. The study showed that, the liquid products decreased linearly from 53.1 – 47 wt.% whereas the gas products increased linearly from 32.4 – 41 wt.% with increasing temperature and heating rate.

## 3.3. RESIDENCE TIME

Residence time is the average amount of time (seconds, minutes, and hours) spent by feedstocks in the pyrolysis reactor which may affect the product distribution [71]. Generally, researchers agree that longer residence times are suitable for the production of syngas through co-pyrolysis. Others have realized the minimum impact of residence times alone on the conversion of materials into syngas as compared to temperature. The impact of residence time and temperature on the gaseous product composition in a fluidized bed reactor from pyrolysis of HDPE was investigated by Mastral et al. [72]. The temperature and residence time varied from 650 – 850 °C and 0.64 – 2.6 s, respectively. They found that the maximum yield of syngas of 86.4 wt.% was obtained at a temperature of 780 °C and a residence time of 1.34 s. Similarly, the roles of residence time and temperature on the pyrolysis of polyethylene and polystyrene on pyrolysis product composition in a closed batch reactor were investigated by Onwudili et al. [73]. It was found that increasing temperature and residence time favoured the conversion of gas to oil in polyethylene. Brems et al. [74] posited that slow pyrolysis leads to the dwindling of bio-oil yields and favours the promotion of char and gas yields due to longer residence times. Önal et al. [75] intimated that the influence of residence time can best be understood when the sweeping gas flow rate is varied while keeping the temperature constant during a process. Also, a study conducted by Xiong et al. [76] revealed that longer residence times not only affect the syngas yield and quality but also the chemical properties of the bio-oil were improved due to the reduction of oxygen-to-carbon ratios (O/C) of the bio-oil. Morgan et al. [77] observed that longer residence times produced less bio-oil and char and higher syngas and volatile yields. Xu et al. [78] studied hydrogen-rich gas production from two-stage catalytic pyrolysis of pine sawdust with Nano-NiO/Al$_2$O$_3$ catalyst. Their results showed that, at longer residence times, the bio-oil and char yields decreased whereas gas yield increased. Further, the H2/CO ratio, carbon conversion, gas-phase conversion reactions, and tar cracking were all improved due to the longer residence times.

## 3.4. ADDITION OF CATALYSTS

A catalyst can be defined as a substance that accelerates the rate of chemical reactions without being consumed at the end of the process. This result is achieved by lowering the

activation energy of the process. It is noteworthy that catalysts can take a different pathway to obtain the end product, thereby affecting the yield and selectivity. The application of catalysts in co-pyrolysis reduces the optimum temperature and time required to complete the process thereby saving energy in the chemical industry [9,22]. Several pieces of research have been published on the role catalysts play in the enhancement of co-pyrolysis product distribution using different catalysts including cobalt-based alumina, ceria, and ceria alumina catalysts [79]; mesoporous Al-SBA-15 catalyst [1]; Ni-Fe@Nanofibers/Porous carbon catalyst [2]; cobalt-modified ZSM-5 catalyst [80]; metal-modified zeolite catalyst [43]; nickel-activated carbon catalyst [40]; Ga-MFI zeolite catalyst [81]; and Fe/CaO catalyst [65]. According to Uzoejinwa et al. [82] and Anuar Sharuddin et al. [71]: zeolites, FCC, and silica-alumina catalysts are the three main catalysts used in lignocellulosic and plastic materials co-pyrolysis. Of the three catalysts, zeolite is the most used. Catalytic co-pyrolysis of biomass and plastics has been examined by Chattopadhyay et al. [79] in a fixed bed reactor using Co-based catalysts to analyse the product distribution and selectivity. In their study, it was found that the syngas yield was maximum at a biomass/plastic ratio of 5:1 in the presence of 40 % Co/30 % CeO2/30 % Al2O3 catalyst. Xiang et al. [80] investigated the thermal behaviour and kinetic study of rice straw and linear low-density polyethylene co-pyrolysis over Cobalt modified ZSM-5 catalyst and found that the catalyst was able to lower the activation energy and the reaction rate was improved. Al-asadi et al. [43] observed that the syngas yield from plastic pyrolysis-gasification was significantly improved using metal-modified zeolite catalysts. In their study, the maximum syngas yield was obtained at a temperature of 850 °C and with lanthanum catalyst of proportion 112.2 mmol/g (95%N2 and 5%O2), and 130.7 mmol/g (90%N2 and 10%O2). Bobek-Nagy et al. [40] performed catalytic co-pyrolysis of packaging plastic and wood waste to achieve hydrogen-rich syngas and found that the optimum concentration of hydrogen was 392.8 mmol/g sample using 10% Ni-AC catalyst.

## 3.5. TYPE OF FEEDSTOCK

As mentioned earlier, the quantity and composition (quality) of syngas are highly dependent on the type of feedstocks used for the co-pyrolysis process. As such, it is imperative when it comes to the selection and availability of feedstocks for the co-pyrolysis process as this influences the outcome of the final product. In this section, the emphasis is laid on reviewing the literature to know the significance and influence of both lignocellulosic biomass and plastics on the final product (syngas) of co-pyrolysis.

### 3.5.1. EFFECT OF LIGNOCELLULOSIC BIOMASS COMPOSITION ON SYNGAS PROPERTIES

Lignocellulosic biomass (wood, agricultural, and forestry residues) is the non-edible part of plant materials consisting of three major compounds: lignin, hemicellulose, and cellulose [63]. Among the three, cellulose and hemicelluloses produce most of the volatile matter with cellulose being more volatile than hemicellulose [9,83]. According to Zhang et al. [84], it comprises traces of extractives and inorganic minerals (Ca, K, Mg, Si, P, Na) in addition. Typical biomass has the following range of lignin (15 – 30 wt.%), hemicellulose (15 – 40 wt.%), and cellulose (30 – 60 wt.%) composition on a dry basis [85].
Table 1 shows the percentage composition of each compound within softwood and hardwood biomass for biofuel conversion. It should however be noted that the yields of pyrolysis products differ as a result of the lignocellulose content in the selected biomass. This is because, during pyrolysis, the chemical structure and composition of every biomass differ in their thermal degradation and chemical transformation [84].
Wang et al. [86] conducted a research on the pyrolysis of sawdust and its three components: lignin, hemicellulose, and cellulose using a thermogravimetric analyzer under syngas and

hydrogen. Their observation was in concordance with the previous authors as it was found that hemicellulose was the easiest one to be pyrolyzed followed by cellulose and lignin and this phenomenon was linked to their chemical structures. Co-pyrolysis of plastic wastes (PE, PP, PS) and pine biomass was studied by Paradela et al. [56]. They found that the main compounds of the gaseous products were alkanes, alkenes, CO, and $CO_2$. Furthermore, the char and gaseous fractions increased proportionally with the pine percentage whereas the liquid yield decreased. This is in broad agreement with a study conducted by Wang et al. [20]. In their study, the waste tire was co-pyrolyzed with pine bark to produce syngas and char under an $N_2$ atmosphere at 900 °C. Results showed that the peak flow rate of $H_2$, CO, and total syngas yield increased with increasing pine bark in the mixture.

**Table 1. The difference in biomass constituents among vascular plants (softwood, hardwood, and grasses).[1]**

| Biomass constituent | Dry weight (%) |
|---|---|
| Cellulose | 15 – 49 |
| Hemicellulose | 12 – 50 |
| Xylan | 5 – 50 |
| Mixed-linkage glucan | 0 – 5 |
| Xygloglucan | Minor |
| Mannan (and galactoglucomannan) | 0 – 30 |
| Soluble (mainly sucrose) | 9 – 67 |
| Pectin | <0.1 |
| Lignin | 6 – 28 |
| Ferulic acid and *p*-coumaric acid | <1.5 |
| Protein | 4 – 5 |
| Ash (mainly silicate) | 0.4 – 14.4 |
| Intrinsic moisture | 11 – 34 |

[1]Adapted from Lin et al. [87]

## 3.5.2. EFFECT OF PLASTIC COMPOSITION ON SYNGAS PROPERTIES

Plastics are polymeric materials that can easily be transformed into different shapes when heated. They are long-chain hydrocarbons with sometimes hydrogen, sulfur, oxygen, and nitrogen elements present depending on the composition of the plastic type. According to how they behave when heated, they can be categorized as thermoplastics and thermosets [88,89]. The most commonly used thermoplastics are polyethylene/polythene (PE), which can further be classified as high-density polyethylene (HDPE) and low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinylchloride (PVC) [74,90–92]. Figure 2 shows the monomers of the foregoing polymers.

The good news is that these plastics are made from petroleum products and possess enough chemical energy which can be utilized to meet the global energy crisis [93]. It should be noted that the thermal decomposition of the polymer mixtures is cumbersome as compared to the decomposition of single polymers. This is because of the interactions during the cracking of the polymer bulk and that of the interactions between the components of the mixture as well as the low molecular weight products and free radicals formed by the scission of the polymeric chains [94,95].

Williams and Williams [95] performed the pyrolysis of six separate thermoplastics and their mixture using a fixed bed reactor at a temperature and heating rate of 700 °C and 25 °C/min,

respectively. Results showed that PET gave the highest volume of syngas. In a similar vein, authors such as Brebu, Çepelioğullar and Pütün, and Fakhrhoseini and Dastanian corroborated the claim that PET and/or PVC gives the highest volume of gas when pyrolyzed. Brebu et al. [94] found that the presence of PVC and PET in the polymer mixture (PE, PP, PS, ABS-Br) dwindled the amount of bio-oil yield while increasing the amount of gas produced. Çepelioğullar and Pütün [96] investigated the utilization of PET and PVC as feedstocks in pyrolysis using a fixed bed reactor at a temperature of 500 °C to produce the solid, liquid, and gas products. It was found that the amount of gas PET produced was 76.9 wt.% whereas that of PVC yielded 87.7 wt.%. Fakhrhoseini and Dastanian [97] predicted the pyrolysis products of PE, PP, and PET using the NRTL Activity Coefficient Model. The process was maintained at 500 °C and was discovered that PET yielded the highest gas percentage (65.12 wt.%) at a heating rate of 14 °C/min.

## 3.6. TYPE OF REACTOR

Several reactor types have been designed and fabricated for the production of pyrolysis products, each with its own set of characteristics, depending on the plant, to optimize product yield and quality while minimizing costs and environmental effects. Pyrolyzing units can be categorized as fixed bed reactors, fluidized bed reactors, and screw kiln reactors based on the mode of heat transfer and flow arrangements of the feedstocks and final product delivery [98]. According to Abnisa and Wan Daud [9], most studies on co-pyrolysis employed the fixed bed reactor. Also, according to Anuar Sharuddin et al. [71], the fixed bed reactor is explored mostly at the lab-scale level because it is easy to construct, affordable, flexible control of operating parameters, and easy to renovate. At the commercial scale level, the fixed bed reactor is seldom used due to factors such as low heating rate, and irregular temperature distribution within a large sample size, among others [99]. This is in broad agreement with what was observed by Couto et al. [100]. On the contrary, Raza et al. [101] reported that fixed bed reactors are the most common and important reactor type used in the process industry and for the production of chemicals and intermediates on a large scale. It has the following major components: stationary bed (reactor), condenser, heating element, and collectors [102–104]. It is noteworthy that the synergistic effect is highly dependent on the extent of contact between the selected feedstocks. Therefore, the synergistic effect is likely produced when the feedstocks are pyrolyzed in a fixed bed reactor than in a fluidized bed reactor [105].

Jin et al. [106] performed synergistic effects of biomass and plastic co-pyrolysis on gas, tar, soot, and char production and pyrolysis kinetics were studied using a fixed bed reactor and thermogravimetric analyzer, respectively. They found that the synergistic effect observed using the thermogravimetric analyzer agrees with the one in a fixed bed reactor at 800 – 1100 °C.

## 4. CO-PYROLYSIS OF BIOMASS AND PLASTIC MATERIALS

Co-pyrolysis is a thermochemical process that uses more than one feedstock – biomass and plastics/waste tires – to produce an improved pyrolysis product (solid, liquid, and gas) due to the synergistic effects [9]. Co-feeding of biomass and polymers presents several opportunities over mono-pyrolysis because of its simplicity, effectiveness, and above all the synergy that results from the interaction of different feedstocks [82]. Table 2 highlights the findings from other reports on the co-pyrolysis of biomass and plastics to produce syngas. It should be pointed out that the key operating conditions including temperature, heating rate, residence time, and catalysts always affect the syngas production positively. As discussed in sections 3.5.1 and 3.5.2, biomass is composed of cellulose (a polymer glucosan), hemicelluloses (which are also known as polyose), and lignin [54]. Among the three, cellulose and hemicelluloses produce most of the volatile matter [9] with cellulose being more volatile than hemicellulose [83]. Cellulose is the prime structural component of plant cell walls [63] with a high molecular weight (106 or more) linear polymer of $\beta$-(1→4)-D-

glucopyranose units [54]. The thermal decomposition of cellulose occurs at ~320 – 400 °C [107] to produce levoglucosan, levoglucosenone, hydroxymethylfurfural, furfural, hydroxyacetaaldehyde, and acetic acid [90]. In contrast, Mohan et al. [54] found that the thermal decomposition of cellulose normally happens at a temperature range of 240 – 350 °C to produce anhydrocellulose and levoglucosan. Hemicellulose disintegrates at a temperature range of 200 – 260 °C. Also, hemicelluloses produce more volatiles, fewer tars, and chars as compared to cellulose. Lastly, lignin normally decomposes at 280 – 500 °C yielding more chars as compared to cellulose. According to Sogancioglu et al. [13], plastics are manufactured from petroleum products and consist of hydrocarbons. Plastics are grouped into thermoplastics and thermosets. The thermoplastics are the ones widely explored which include polyethylene terephthalate (PET), high and low-density polyethylene (HDPE & LDPE), polyvinyl chloride (PVC), polystyrene (PS), and polypropylene (PP) [91]. Paradela et al. [56] and Wang et al. [20] observed that when the biomass concentration is higher in plastic co-pyrolysis, the syngas yield and quality are improved whereas the bio-oil yield is decreased.

**Table 2. Summary of results from literature sources on co-pyrolysis of biomass and plastics to obtain syngas**

| Feedstock type | Operating conditions | | | | Findings | Ref. |
|---|---|---|---|---|---|---|
| Biomass/plastic | Temp. | Heating rate | Residence time | Catalyst | | |
| Hazelnut shell/PE | √ | - | - | - | At all temperatures and compositions, the co-feeding of the feedstocks favour the production of gas to liquid. | [108] |
| Potato/HDPE | √ | √ | √ | - | At longer residence times, the syngas yield increased whereas the bio-oil decreased. | [76] |
| Pine sawdust/HDPE | √ | - | - | √ | $H_2$-rich syngas with up to 33.6 mmol $H_2$/g biomass and tar yields as low as 5.66 mg/g was recorded at 700 °C using bimetallic NiFe@CNF/PCs catalyst. | [2] |
| Sugarcane bagasse/LDPE | √ | √ | - | - | It was observed that the gaseous products increased over the whole temperature range because of further decomposition of the light liquid components. | [22] |
| Paper/PS | √ | - | - | - | Syngas yield and quality were improved due to the synergistic effects resulting from paper and PS. Also, the hydrogen concentration was doubled. | [19] |
| Pine bark/waste tire | √ | - | - | - | The peak flow rate of hydrogen, carbon monoxide, and total syngas yield increased with an increase in pine bark in the mixture with only $C_mH_n$ decreasing. | [20] |

√ Reported, ⁻ Not reported.

## 5. MECHANISM OF CO-PYROLYSIS OF BIOMASS AND PLASTIC MATERIALS

According to Uzoejinwa et al. [82], the underlying concept behind the co-pyrolysis methodology is the induced synergistic effects resulting from the interaction between two or more feedstocks producing an end product with an effect more than the sum of the individual components. Hassan et al. [109] posited that the synergistic effects resulting from the intermingling of biomass and plastics are attributed to the radical interaction during co-pyrolysis. Plastics and artificial polymeric material progress as a radical interaction comprising radical initiation, chain propagation/secondary radicals' formation, and termination by radicals' disproportionation or recombination while biomass takes a different approach which is characterized by a series of both exothermic and endothermic reactions [9,13,47]. It is noteworthy that factors such as high moisture content, pH, and high oxygen content in biomass affect the overall chemical composition and properties of the pyrolysis products when pyrolyzed alone [110,111]. On the other hand, plastics are very rich in hydrogen and thus co-pyrolyzing with biomass improves the syngas yield and quality [19]. Xue et al. [110] studied the role of temperature and co-feeding of biomass with HDPE in a lab-scale fluidized bed reactor. They found that increasing pyrolysis temperature increases the oil yield with a further increase in temperature, resulting in the breakdown of the oil to form light gases rich in hydrocarbons. It was also found that the synergistic effects during co-pyrolysis were pronounced. Ephraim et al. [47] investigated the synergistic effect of PS, PVC, and poplar wood on the product yield, gas species yield, and heating value. They found that the addition of PS positively impacted the gas species yield by promoting the formation of $H_2$, $CO_2$, $CH_4$, and CO. Other pyrolysis end products including the bio-oil and char products were all affected positively. Johansson et al. [111] found that the co-feeding of biomass and plastics significantly affected the composition and properties of the products. Furthermore, they observed that the establishment of hydrocarbons was encouraged whereas biomass oxygenated compounds such as ketones, aldehydes, etc. dwindled due to the synergistic effect.

## 6. CONCLUSION

This review presented the opportunities of using syngas as an alternative renewable energy source to complement the already depleting fossil fuel reserves. Syngas quality and yield can be optimized by carefully manipulating the operating conditions such as temperature, residence time, heating rate, and catalyst during co-pyrolysis. Several literature works have been reviewed and discussed buttressing all points listed in this paper. Biomass and plastics are copiously available everywhere in the world making the co-pyrolysis technology a sustainable approach to producing syngas which can be used to fuel gas turbines and engines to produce electricity, among others. Besides, the burden of most developing countries for treating municipal solid waste can be solved using co-pyrolysis technology. The technology does not only improve the composition and quantity of syngas alone but also the bio-oil and char products are significantly improved owing to the synergy that co-exists between the feedstocks.

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