



2nd International Conference on Sustainable Materials Processing and Manufacturing
(SMPM 2019)

Effects of biomass/coal copyrolysis parameters on the product yield: a review

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Abstract

Pyrolysis is one of the prospective processes that can be utilized to obtain high value chemicals and energy from coal and biomass. Coal-biomass co-pyrolysis presents a green, low-risk, cheap, sustainable, renewable energy source with low carbon emissions. Co-pyrolysis offers the highest yield of liquid fuels and gas compared to the individual feedstocks. It has been illustrated that the production yields experimentally usually exceed the calculated and this can be explained by the possible synergy and interactions that takes place when coal is blended with biomass. The progressive OH and H ions donated to coal from biomass together with the catalytic function of AAEM species (mainly K, Na, Ca, and Mg) could explain this synergetic effect from the biomass. The yield, composition and distribution of coal-biomass co-pyrolysis products is largely dependent on operative parameters. Therefore, it is very important to explore the effects of these variables on product yield. Parameters influencing coal-biomass pyrolysis include feedstock type, feedstock pre-treatment, and reaction conditions i.e. catalysis, temperature, residence time and heating rate. This written material outlines a concise product properties due to the variable pyrolysis conditions together with product analysis methods.

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Peer-review under responsibility of the organizing committee of SMPM 2019.

Keywords: Coal-biomass co-pyrolysis; product yields; distribution; synergy; pyrolysis parameters

1. Introduction

Lately biomass production and exploitation has attracted much attention as an energy resource. This is because of concerns associated with global warming and depletion of fossil fuels. Biomass presents a carbon neutral energy resource i.e. it produces a zero-net due to carbon offsetting hence limited effect on the ozone layer [1]. The challenge with burning biomass directly is that, the process will present minimal energy transformation efficiency due to its low heating value. In order to increase the energy efficiency as well as product yield, biomass is blended with other fuels thermo-chemically in an economically attractive way, in this case coal [2].

Coal is known to be the most voluminous fossil fuel worldwide and the cheapest for its energy content. It supplies a third of all the energy utilized around the world, see Fig. 1 below predicting coal demand. Although coal production has its major downfalls such as air pollution and greenhouse emissions, immense efforts are been implemented to

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determine processes and technologies of low pollutants and cleaner energy production systems such as the one outlined above being co-pyrolysis of coal and biomass [3].

Nomenclature			
AAEM	Alkali and alkaline earth metallic species	H/C	Hydrogen/carbon ratio
Ca	Calcium	K	Potassium
CB	Corncob	Mg	Magnesium
CO	Carbon monoxide	OH	Hydroxide ion
CO ₂	Carbon dioxide	R-O-R	Ether functional group
C=C	Carbon to carbon double bond	SD	Sawdust (pine)
DTG	Differential thermo-gravimetric	TF	Tiefa bituminous coal
DY	Dayan brown coal	TG	Thermogravimetric
H	Hydrogen ions	YL	Yilan sub-bituminous coal
HDO	Hydrodeoxygenation		

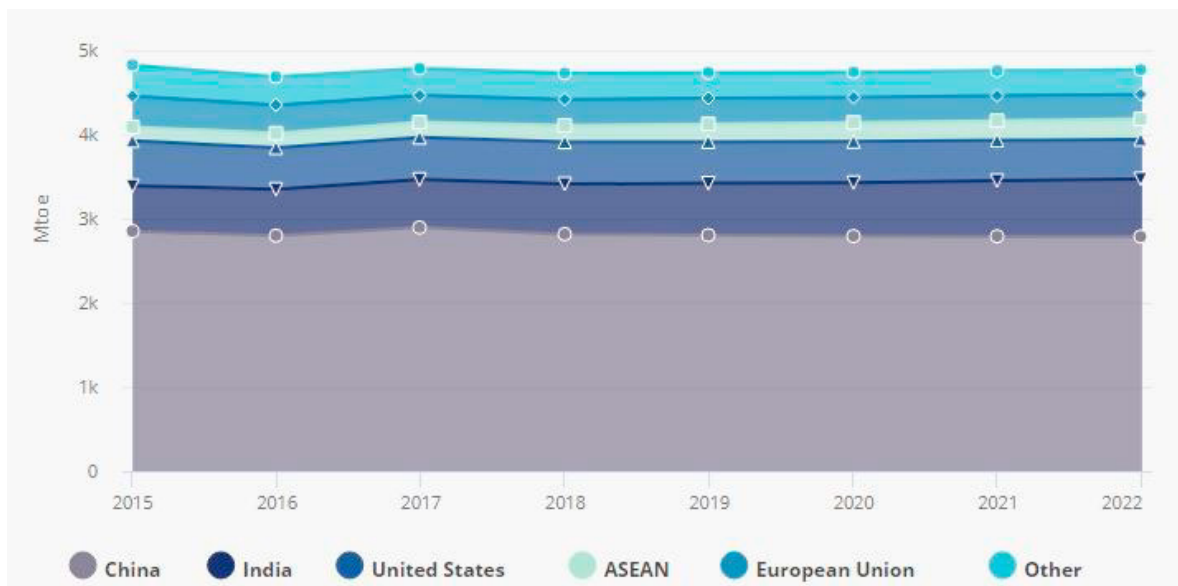


Fig. 1: Coal demand forecast 2016-22. Source market series report: 2017 [3]

Coal pyrolysis is a prospective process that can be effectively used for the production of liquid fuels and synthetic gases. Nonetheless coal has low quantity and quality these yields due to low H/C atom ratio. It is therefore, this reason that coal and biomass co-pyrolysis is used as an efficient process to enhance product yield [3]. Extensive research on biomass and coal co-pyrolysis is ongoing worldwide and improvements on the products by interactions and synergy have been discovered experimentally [4]. TG analyzer have been used to prove the synergy during copyrolysis of biomass together with coal by Shang et_al [5] and Wu et_al [6] and alternatively Senobe et_al [7] and Park et_al [8] confirmed the synergy in a fixed bed reactor.

As mentioned above, broad, argumentative work on the influence of synergy on the product yield during copyrolysis is going on; it is not yet clear that only the synergy from primary pyrolysis or secondary reactions of volatiles due to

long residence times [3]. These discrepancies may also be affected by different factors such as temperature, heating rate, blending ratio, feedstock type and type of catalyst [9].

2. The mechanism of co-pyrolysis process

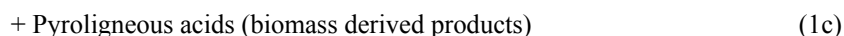
2.1. Theory and background

Alternative methods can be utilized to convert coal to multipurpose products. Amongst them is combustion which is the most predominate process in coal exploration. Nevertheless, other technologies have emerged in this regard after considering the downfall of coal combustion such as release of CO₂ and CO due to excess air supply or insufficient air respectively. These technologies include pyrolysis, liquefaction, carbonization and gasification [10, 11]. Pyrolysis offers a very important site in coal technologies because through it production of tar, coke and gases is abridged sustainably. Nonetheless, pyrolysis of coal produces limited liquid yields due to its low H/C ratio. It is therefore important to source additional hydrogen in order to upgrade the liquid products [12]. biomass/coal copyrolysis offer great advantages to both the biomass and coal product yield i.e. biomass contains high hydrogen content that is required by coal during pyrolysis for increased liquid product yields and similarly, biomass has limited energy density as a result of oxygen and moisture content which is then overcame by blending with coal [13]. Co-pyrolysis adds the beneficial aspect of biomass to coal as biomass produces fuels that are carbon neutral, hence reducing the CO₂ footprint. This aspect brings about a cleaner coal utilization and a easier path to increase the quality and quantity of pyrolytic products [14].

Normal pyrolysis and co-pyrolysis mechanisms have no significant difference. The process involves heating the samples at intermediate temperature in the absence of oxygen in a closed reactor. In terms of liquid and syngas production from pyrolysis, three common steps required include the following:

- ✓ Sample preparation
- ✓ Co-pyrolysis
- ✓ Condensation [15]

The pyrolysis process respond to reactions related to devolatilisation and/or thermal decomposition that takes place at the primary stages during heating of solid samples at an intermediate temperature. The following gives a general representation of pyrolysis [16];



Different parameters affect the volatile matter yield. Amongst them is temperature and heating rate. Higher temperature leads to elevated syngas production. The additional gas yield is from the secondary cracking of primary products. Conversion of pyrolygneous acids takes place as the temperature increases [16]. As a way of intensifying the efficiency in application of the pyrolysis liquids and gas, improvements in the reaction process is vital. Vast studies have been done regarding upgrading techniques that can counteract the high oxygen content and moisture. Amongst them is the catalytic cracking and HDO [17]. Catalytic cracking involves addition of an appropriate catalyst in the pyrolysis reactor while HDO is upgrading of the pyrolytic oils into hydrocarbons [18].

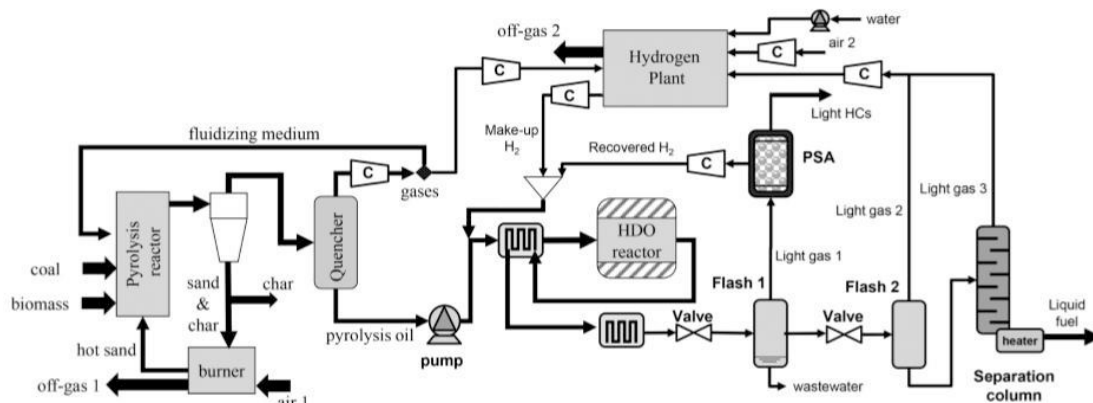


Fig. 2: Typical flow diagram of pyrolysis oil, liquids and gas production during biomass/coal co-pyrolysis [10]

The co-pyrolysis process diagram is shown in Figure 2 above, showing coal and biomass being fed and a mixture of products (oil, char and gases) in the outlet of the reactor. It also shows post refinery processes as well as potential applications.

3. Sustainability of pyrolysis process

As already mentioned above pyrolysis process is dependent on several properties such as temperature, feedstock type, heating rates, moisture contents of feed samples. The process needs to be optimised in order to attain high quality products.

Nevertheless, pyrolysis process is a simple method that can be utilised in various locations around the world even at remote areas as a way of promoting energy sustainability from biomass feedstocks. It is a reliable and flexible system that is easy to manipulate in terms of operating parameters. Products from pyrolysis process are well defined and can be successfully be utilised in chemical industries as well as power and heat production processes. Moreover pyrolysis is an accommodating process as vast biomass feedstocks such as cow dung, rice husks, wood chips etc can be used to produce the required liquids and gas products. It can be performed at different rate i.e.

- Fast pyrolysis: To produce mainly bio-char which may further be utilised in gasification process downstream
- Slow pyrolysis: To produce mainly bio-oils and syngas [49].

4. Parameter effects on product yield and characteristics

4.1. Effect of feedstock type

The kind of feedstock used for co-pyrolysis largely influences the product yield. Any type of feedstock poses synergy during co-pyrolysis and this can lead to increase liquid yield at a particular conditions. Different authors have done experiments to determine the effect of different kinds on biomass and coal. Li-Gang, Wu et al, [3] has discovered that during co-pyrolysis of pine sawdust and Tiefs bituminous coal, SD/TF the experimental liquid yields of about 6.4% higher than the calculated value i.e compared to 2.6% variation on the experimental and the calculated value during pine sawdust and Dayan brown coal SD/DY co-pyrolysis for similar parameters i.e. 600°C and 70 w/% as shown in table 1. Experimental and calculated yields of tar shows no significant difference during copyrolysis of either TF or DY. It can be concluded synergy takes place when blending biomass with TF than DY as a result of the differences in coal ranks [19].

Table 1: Effect of blending SD/DY co-pyrolysis on the product output [19]

Temperature t /°C	Blending ratio w /%	Yield w_{daf} /%							
		gas		liquid		tar		char	
		exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
500	0	6.7	6.7	33.9	33.9	3.6	3.6	60.3	60.3
	25	15.3	15.1	35.2	35.6	6.7	6.2	48.4	49.5
	47	22.5	22.5	36.3	37.1	9.4	8.4	39.3	40.0
	71	28.0	30.5	40.8	38.7	15.9	10.9	27.6	29.6
	72	28.5	30.8	40.9	38.8	14.7	11.0	27.2	29.2
	100	40.2	40.2	40.7	40.7	13.9	13.9	17.1	17.1
600	0	6.7	6.7	36.2	36.2	5.1	5.1	53.1	53.1
	26	20.4	19.8	35.9	35.0	8.2	6.0	42.5	42.0
	50	30.1	31.9	34.8	33.8	8.4	6.9	30.8	31.8
	70	40.2	42.0	35.5	32.9	9.5	7.6	21.8	23.3
	100	57.1	57.1	31.4	31.4	8.7	8.7	10.5	10.5
700	0	15.5	15.5	30.7	30.7	5.8	5.8	48.4	48.4
	29	29.7	31.3	29.4	29.3	5.9	5.2	36.5	35.8
	54	43.2	44.9	30.2	28.0	5.0	4.7	24.1	24.9
	67	48.7	52.0	30.6	27.4	5.3	4.5	17.0	19.3
	100	70.0	70.0	25.7	25.7	3.9	3.9	4.9	4.9

Table 2: Effect of blending SD/TF co-pyrolysis on the product output [19]

Temperature t /°C	Blending ratio w /%	Yield w_{daf} /%							
		gas		liquid		tar		char	
		exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
500	0	1.6	1.6	13.3	13.3	4.0	4.0	87.2	87.2
	50	19.3	20.9	30.1	27.0	9.0	9.0	50.3	52.1
	70	26.8	28.6	36.9	32.5	11.9	10.9	36.2	38.1
	100	40.2	40.2	40.7	40.7	13.9	13.9	17.1	17.1
600	0	3.5	3.5	20.7	20.7	7.9	7.9	74.7	74.7
	45	25.2	27.0	29.7	25.5	8.2	8.3	38.9	45.8
	70	40.2	40.7	34.6	28.2	12.5	8.5	24.0	29.7
700	100	57.1	57.1	31.4	31.4	8.7	8.7	10.5	10.5
	0	11.1	11.1	21.1	21.1	6.9	6.9	63.5	63.5
	42.5	34.7	36.1	25.6	23.1	6.1	5.8	36.4	38.3
	70	49.6	52.3	28.0	24.3	6.4	5.0	18.6	21.4
	100	70.0	70.0	25.7	25.7	4.2	4.2	3.0	3.0

4.2. Effect of blending ratio

During co-pyrolysis, it has been shown that the amount of biomass blended with coal affects the amount of pyrolytic products (liquids and gases) by [20]. [21] has discovered that as biomass feedstock is increased in the coal feed during pyrolysis, the rate of production of syngas and liquid fuels increases whereas the char and tar production are decreased. Vast researchers have also found out that on the TGA the percentage residual mass decreases as the biomass amount increases more than the individual feedstocks [21, 22, 23, 24]. The evidence from the above conclusions is shown in the figure below showing change in oil, gas and char yields at different biomass ratios.

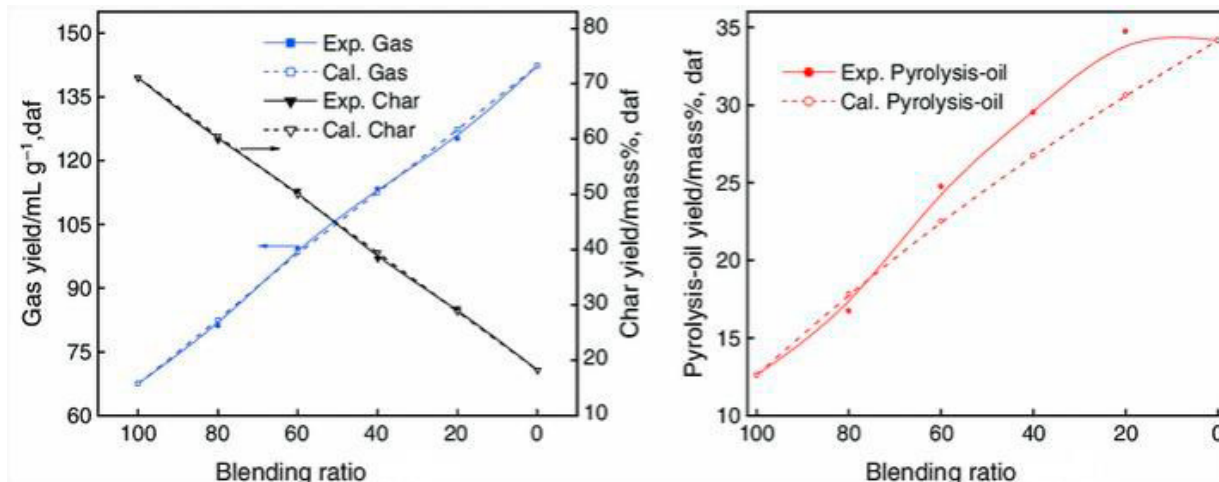


Fig. 3: Oil, gas and char yield at different blending ratios [21]

Authors [25, 26, 27, 28] also did experiments on the co-pyrolysis on TG to investigate the mass loss for different feedstocks. And found out that the coal feedstock structures is made up of vastly cross linked aromatics that are very difficult to break at low temperature. This is because coal structures are held together by strong carbon to carbon double (C=C) bonds. Biomass macro-molecular structures on the other hand is made from relatively weak ether bonds (R-O-R) that break easily on heat, therefore biomass decomposes faster than coal. When biomass is blended with coal, it will transfer the H and OH radicals to coal in order to assist in the breakage of the aromatic linkages. This increase the liquid fuel and gas yields and lower char production. Figure 4 below is what was found from the TG showing increased mass loss at 50-50 coal-biomass ratio.

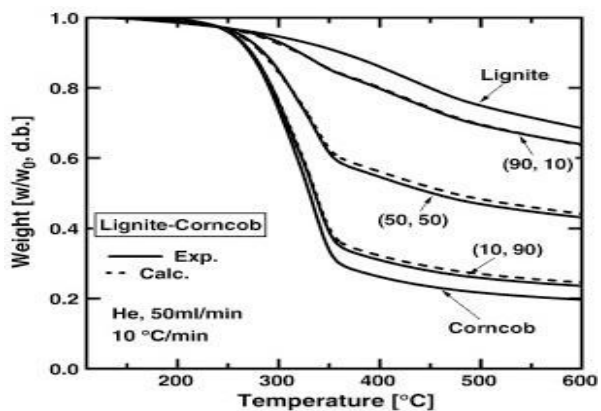


Fig. 4: TG analysis for individual and blended feedstock[25].

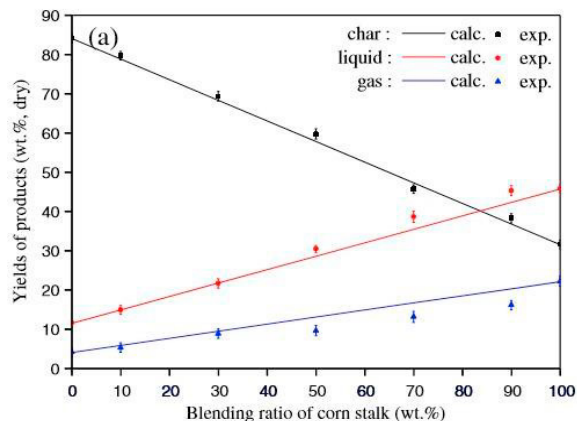


Fig. 5: Products yield as a function of blending ratio [29].

In addition, Min Guo and Ji-Cheng Bi [29] also suggest that across the blending ratio at different temperature, the char output during co-pyrolysis is equals the calculated values as shown in Figure 5. [29] demonstrates that only a slight change is noticed in the liquid yields from the experimental to the calculated amount. This can be concluded that synergy is only taking place on the volatiles but not char.

Contrary to the findings made from the authors about the importance of blending biomass with coal in order to promote high gas yields and low char yield, [30, 31] argues that on a drop tube at high heating rates, the amount of volatiles being liquids and water produced from blending woody biomass and coal is relative to the combining ratio. The

proportionality implies zero chemical reactions took place during the process hence no synergy observed. Fig. 6(a,b,c) show how production of char, tar and liquid fuels changes with blending ratio. It can be concluded that products formed during pyrolysis equals the algebraic sum of the respective fuels explained by a linear product yields and blending ratio [31].

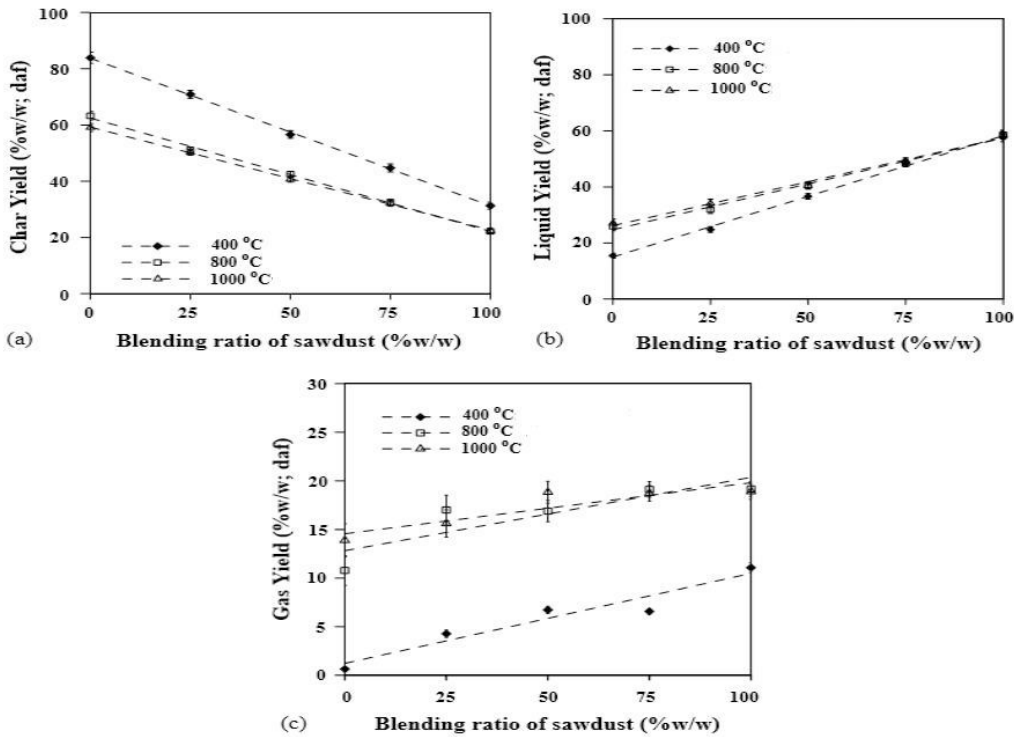


Fig. 6: Outcome of blending ratio of coal and sawdust on char, liquids and gas [31]

4.3. Effect of temperature

Product distribution and product properties are largely affected by reaction temperature during pyrolysis. Coal products are mainly dominated by solids whereas biomass products are dominated by liquids and gases [32]. biomass/coal co-pyrolysis combines the best attributes of both fuels in order to shift the production of solids to liquids with limited production of char and tar. A number of authors [33, 34, 35, 36, 37] have found out that with temperature increase char yields decrease while the production of volatile matter increase i.e pyrolysis conversion increase with increasing temperature because of the greater decomposition of the samples. It has been found that biomass promote the devolatilisation of coal mainly at low temperatures. Aboyade et al [38] has found out that at temperatures between 300 and 400°C synergy and interactions of coal/biomass blend corresponds to biomass devolatilisation ending and the initiation of coal decomposition starting. Ulloa et al [39] has established that at temperature of about 400°C is where major interactions takes within the samples and as temperature increase secondary reactions take place leading to limited char production. Zhang et al [40] did a study in a free fall reactor to establish the optimum volatile matter yields and found out that synergy and interaction for higher production is at temperature of 600°C in the co-pyrolysis of lignite and legume straw. At this temperature, it is suggested that there is enough formation of free radical and hydrogen donors from biomass to coal.

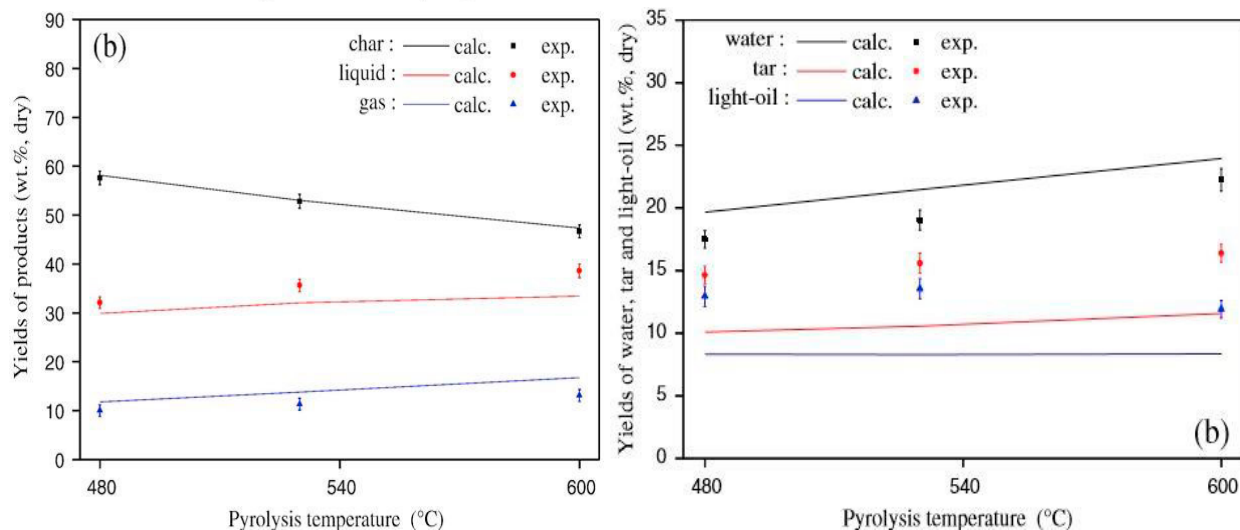


Fig. 7: Influence of temperature on product output at a biomass blending ratio of 70% [29]

The rate of product formation is slow due to small temperature range. The occurrence of synergy, with increasing temperature during co-pyrolysis leads to the experimental yields being higher than the calculated yields while the char and water decrease with increasing temperature (Figure 7). Continuous increment in temperature limit synergy because the pyrolysis rate increase while the hydrogen donating ability is limited leading to retrogressive condensation reactions being favoured [40].

4.4. Effect of heating rate

Heating rate has shown to impact positively and negatively the composition and yield of derived products. Jianfei W et al [41] and Wang G et al [42] performed experiments to determine the effect of heating rate of co-pyrolysis of YL and CB on a TG. As the heating rate increased, the charts of DTG and TG diverted to an elevated temperature region and so the maximum value for the rate of mass loss increased. They found out that at a heating rate of 10 K min^{-1} , the value of maximum mass loss of YL to be -0.21 min^{-1} at temperature of 722 K . This value increased to about -0.59 min^{-1} at temperature of 759 K for a heating rate of 40 K min^{-1} . As for CB, the peak temperature recorded were 590 to 611 K at maximum mass loss moving from -0.092 to 0.311 min^{-1} for heating rate from 10 – 40 K min^{-1} as shown in figure 8 below. As the heating temperature increased, the time to reach pyrolysis temperature is shortened and this is ideal for pyrolysis.

Di Nola, G et al [43] also did experiments to investigate the influence of heating rate on product yield. Experiments were done at heating rate of 10 , 30 and 100 K min^{-1} and the results give that for the samples reactions, there was a side shift in the thermograms towards higher temperatures. They also found out that there is insignificant impact by changing heating rate on char and gas produce for biomass samples used. Coal showed a slight increase of gas yield and slight decrease in char yield as heating rates increased. The reason for char yield's independent relation to heating rates is because the mechanism of cleavage bond breaking, cross-linking and repolymerisation are at equilibrium at those pyrolysis conditions.

Behdad Moghtaderi [44] and Ozlem Onay [45] state that the yield of the main gas species and pyrolysis oil in the product stream are dependent on heating rate. Figure 9 illustrates that when the heating rate was elevated from 2 – 20 K min^{-1} the yields increased. However, heating rates above 20 K min^{-1} showed no effect on the total yields.

Accidental fires from pulverisers of typical PF boilers may be caused by low heating rates of coal/biomass copyrolysis and this needs further investigations.

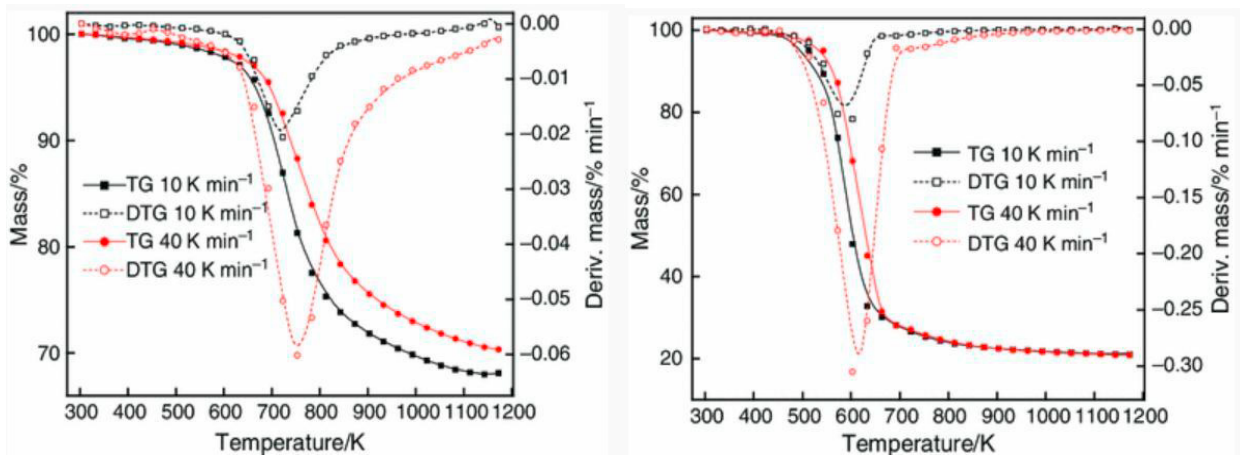


Fig. 8: Charts for DTG and TG curves for YL and CB at heating rates of 10 and 40 K/min [42]

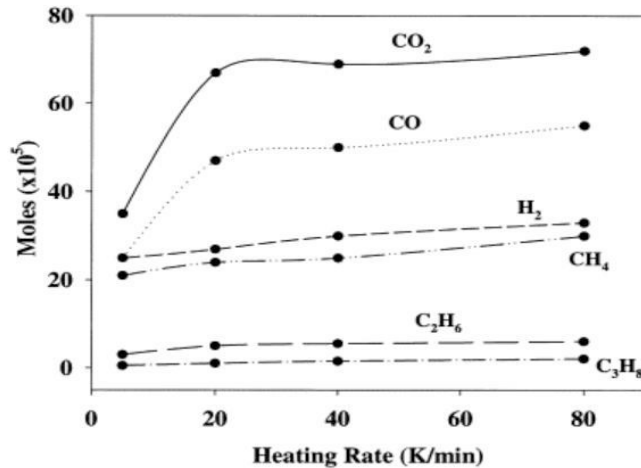


Fig. 9: Total gas yield versus heating rate at 700°C for a 5% blend ratio [44].

4.5. Effect of the catalyst

The catalyst consequence/impact in the co-pyrolysis product distribution and composition of biomass and coal is very important. It can be used to enhance the process economics coal. Not only does catalysis increase the yield of pyrolytic oils, it also promote high value products like aromatics [46]. Maschio et al, 1994 researched the effect of a catalyst during co-pyrolysis and found out that the gas yield was not affected by the catalyst but rather the composition was highly influenced. They found out that the amount of H₂ has increased while CO decreased and organic compounds reduced drastically [47]. Onay O, 2010 investigated the characteristics of pyrolytic oil during biomass/coal co-pyrolysis reaction of coal and biomass and realised that, using criterion-424 catalyst, the yield of pyrolytic oil increased. Figure 10 below from the investigation shows that. For a 50:50 blend of lignite with biomass without a catalyst the yield recorded was 38.7% compared to 42.6% when the catalyst was used as 5%wt. It can also be acknowledged that there is no fundamental deviation in the char yields for various catalyst ratios. The reason being that the criterion-424 had a limited influence in the pyrolysis conversion [46].

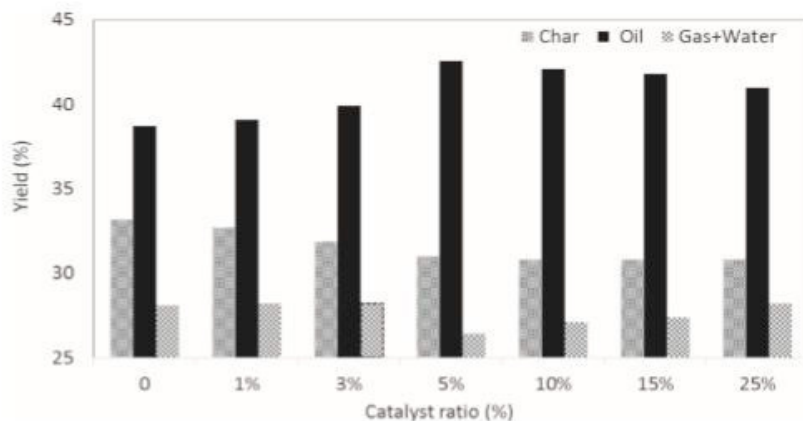


Fig. 10: Effect of criterion-424 catalyst ratio on the production of co-pyrolysis products [46]

As a way of investigating the catalytic outcome brought about by alkali compounds on char production in biomass/coal co-pyrolysis, Wenkui, Z. 2008 [48] acid washed wheat straw to get rid of the Na and K. [48] found out that the char produced from acid washed biomass sample was lower than the raw wheat straw. This is because washing the wheat straw on acid has limited the reactivity of co-pyrolysis char.

5. Conclusions

This manuscript reviewed the determining factor of different pyrolysis parameters on the product yield. Blending of biomass and coal is vital in simulation of synergy that play a major role in promoting production of liquids and gases and reduction in char and tar production. Synergy during co-pyrolysis is usually indefinite, and it is mainly dependent on the pyrolysis method and feedstock used. These contradictory outcomes are fascinating and need to be investigated and explained. The relative deviation and or mass loss shown on TG and DTG analyzers increased as biomass ratio increased. Parameters such as heating rate, pyrolysis temperature range, H/C molar ratio and catalysis has effect on the interaction of biomass and coal as well as product composition and distribution.

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