



Investigation of biomass components on the slow pyrolysis products yield using Aspen Plus for techno-economic analysis

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Abstract

Prior information on the pyrolysis product behaviour of biomass components-cellulose, hemicellulose and lignin is critical in the selection of feedstock as components have a significant influence on the pyrolysis products yield. In this study, the effect of biomass components on the yield of slow pyrolysis products (char, bio-oil and syngas) is investigated using a validated ASPEN Plus® model. The model is simulated at a temperature of 450 °C, a heating rate of 10 °C/min and a solid residence time of 30 min. The results indicated that at the given conditions, lignin contributed 2.4 and 2.5 times more char yield than cellulose and hemicellulose. The hemicellulose contributed 1.33 times more syngas yield than lignin while the cellulose and hemicellulose contributed 8.67 times more bio-oil yield than lignin. Moreover, the cost involved in the production of char using lignin (110 \$/ton) is significantly economical than using cellulose (285 \$/ton) and hemicellulose (296 \$/ton). The net CO₂ emission of lignin pyrolysis is 4.14 times lower than cellulose pyrolysis and 3.94 times lower than hemicellulose pyrolysis. It can be concluded that lignin pyrolysis is more advantageous than cellulose and hemicellulose pyrolysis. In the selection of feedstock for the slow pyrolysis, the feedstock with more lignin content is preferred.

Keywords Cellulose · Hemicellulose · Lignin · Slow pyrolysis · Aspen Plus® · Techno-economic analysis

1 Introduction

Modern society is primarily driven by fossil fuels which contribute towards resource depletion and pollution [1]. The changes in climate, limited and unequal distribution of fossil fuel sources and imbalanced energy trade have increased the importance of alternative sources of energy such as biomass [2, 3]. There is a global impetus to identify low carbon and sustainable sources of energy as agreed by most signatories to the Paris Climate agreement in 2015, for which

the International Panel on Climate Change (IPCC) proposed that bio-energy would be a suitable alternative [4, 5]. Lignocellulosic biomass exists in large quantities as non-edible biomass, mainly composed of forestry and agricultural wastes. It primarily consists of carbohydrate polymers, specifically cellulose (C6-sugars) and hemicellulose (mostly C5-sugars) and lignin [6]. It also contains low amounts of proteins, lipids, nitrogenous compounds, non-structural carbohydrates, waxes, chlorophyll and mineral matter [7]. Cellulose is a linear polymer based on glucose. Hemicellulose is a type of heterogeneous polysaccharide, which contain C6 and C5 sugars. Lignin, on the other hand, is composed of three-dimensional, complex phenylpropane compounds [8]. In addition to these three components, lignocellulosic biomass contains 5–15% of proteins and a small proportion of extractives. The composition of cellulose, hemicellulose and lignin varies from biomass to biomass and is typically in the range of 30–50% (cellulose), 20–40% (hemicellulose) and 10–30% (lignin) respectively [7].

Biomass can be converted into fuels/chemicals by biological and thermochemical conversion processes and it is the only source that can produce solid, liquid and gaseous fuels

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[9, 10]. Amongst the thermochemical conversion processes, pyrolysis is primarily employed for the generation of liquid (bio-oil), gas (syngas) and solid (char) fuels [11, 12]. Pyrolysis is the process of thermal decomposition of organic materials to obtain a set of solid, liquid and gaseous products in the absence of oxygen [13, 14].

Cellulose is a long-chain polysaccharide that exhibits crystalline and amorphous regions. The arrangement of molecules in the crystalline region is uniform and ordered, while in the amorphous region, the arrangement is loose and disordered. The crystalline region of cellulose shows better thermal stability than the amorphous region due to its packed cellulose structure [15, 16]. When cellulose material is subjected to heat during the pyrolysis process, the amorphous region degrades first followed by the crystalline region [17]. On the other hand, hemicellulose is constituted of amorphous structured short-chain heteropolysaccharides such as pentoses, xylose and arabinose. During pyrolysis, the behaviour of hemicellulose is based on those attributes of these building blocks, which turn into a foamy material at higher temperatures resulting in an increase in the char volume [18]. While lignin is made up of aromatic matrices which imparts the strength and rigidity to the plant cell walls. For this reason, the thermal stability of lignin is considerably higher than hemicellulose and cellulose [18]. The decomposition behaviour of biomass pseudo-components was individually investigated by Yang et al. [19]. The decomposition temperature range was observed to be 220–315 °C, 314–400 °C and 160–900 °C for hemicellulose, cellulose and lignin respectively [19]. Among the three components, hemicellulose and cellulose undergo

decomposition easily. However, the decomposition of lignin is a complex phenomenon which can be evidenced by its long decomposition temperature range [20]. When pyrolysed, all these biomass components produce the same gaseous components (CO, CO₂, CH₄ and other hydrocarbons) but with a varying composition, which depends upon the nature of the biomass components and pyrolysis operating parameters. However, a further investigation demonstrated that hemicellulose favours CO₂ yield; cellulose supports CO yield, while lignin encourages H₂ and CH₄ yield. The discrepancy in the behaviour of these components is attributed to the inherent physical and chemical characteristics of these components [21]. Upon pyrolysis, these biomass components apart from generating char, bio-oil and syngas (CO, CO₂, CH₄, H₂) also generate a wider range of products. A few major products of these components and their commercial uses are presented in Table 1.

The pyrolysis of biomass involves a number of complex physical and chemical processing steps to generate a number of products and intermediates [24]. In addition, the pyrolysis process is highly sensitive to thermodynamic properties, operating conditions dependent properties, time-dependent properties and material properties. Hence, modelling and simulation is the best approach to study the pyrolysis process in order to understand the thermochemical reaction mechanism and optimization process. The modelling and simulation studies save both time and cost involved in practical experimentations [25]. Aspen Plus is an advanced system-oriented software for process engineering that enables the modelling of biological, chemical and physical systems [26]. Peters et al. [27]

Table 1 Biomass components and their major products upon pyrolysis [22, 23]

Components	Products	Applications
Cellulose	Levoglucosan	Often used as a chemical tracer for investigating biomass combustion in atmospheric chemistry studies.
	5-HMF	Used as a biomarker and flavouring agent in the food industry.
	Furfural	Used in the synthesis of solvents (Tetrahydrofurfuryl alcohol (THFA)), polymers (Furan resins), fuels and other useful chemicals (Furfuryl alcohol).
	Methyl glyoxal	Used as a medicine in the treatment of cancer.
Hemicellulose	Hydroxyacetaldehyde	Used in the synthesis of Glyceraldehyde.
	Phenols	Used as a precursor to synthesize plastics.
	Cyclic ketone	Used in the production of Nylon (Cyclohexanone).
	Hydroxyacetone	Used as a flavouring agent in the food industry.
	Propanoic	Used in the synthesis of polymers.
	Acetic acid	Used primarily in the production of cellulose acetate, polyvinyl acetate, synthetic fibres, and fabrics.
Lignin	Benzenediols	Used in the synthesis of pesticides, pharmaceuticals and perfumes.
	Catechol (phenol)	Used as a precursor to synthesize pesticides, flavours, and fragrances.
	Methoxyphenol	Used as an intermediate in the synthesis of antioxidants, pharmaceuticals, plasticizers, and dyestuffs.

Table 2 The properties of the individual pseudo-biomass components

Analysis	Cellulose	Hemicellulose	Lignin
Proximate analysis (wt.%) (dry basis)			
Moisture	3.00	3.00	3.00
Fixed carbon	5.75	16.85	32.47
Volatile matter	94.25	83.15	64.66
Ash	0.00	0.00	2.87
Total	100.00	100.00	100.00
Ultimate analysis (wt.%) (dry basis)			
C	41.46	40.69	5.27
H	5.97	5.75	1.10
N	0.07	0.04	33.52
O	52.48	53.49	2.87
S	0.02	0.03	0.00
Cl	0.00	0.00	0.25
Ash	0.00	0.00	56.99
Total	100.00	100.00	100.00
Heating value (MJ/kg)			
LHV	15.36	14.57	24.55
Reference	Ma et al. [18]	Ma et al. [18]	Ma et al. [18]

developed a pyrolysis process using a novel kinetic reaction model based on the lignin, cellulose and hemicellulose in Aspen Plus. The model used a beechwood feedstock with a set of 149 reactions representing volatilisation, decomposition and re-composition steps. The secondary pyrolysis reactions were represented using linear regression to account for the slow and intermediate pyrolysis reactions. The developed kinetic model in Aspen Plus predicted a higher product yield for lignin-rich biomass compared to cellulosic and hemicellulosic biomass.

In another study, Peters et al. [28] used a kinetic reaction mechanism in Aspen Plus to study the effect of feedstock composition (alkali metal, ash, lignin, cellulose and hemicellulose), residence time and temperature on the pyrolysis product yields and composition. A comprehensive model was used to predict the production of bio-oil. The results showed a good agreement with the literature values for a thermodynamic equilibrium model simulated in Aspen Plus to study the lignocellulosic biomass pyrolysis process [29]. The developed model was used to predict the performance of the pyrolysis process considering the process parameters. The results were in good agreement with literature values [29]. Xianjun et al. [30] employed a yield-based reaction model using Aspen Plus to investigate biomass pyrolysis. A compiled FORTRAN subroutine embedded in the yield reactor was used to estimate the yields of the pyrolysis products. The study investigated the effect of temperature on the pyrolysis product yields and composition. The results indicated an increase in the yield of non-condensable gases and a decrease in the yield of char and bio-

oil with an increase in temperature. In addition, the model indicated the utilisation of Aspen Plus to simulate biomass pyrolysis process by showing high agreement with literature experimental values. The life cycle performance of lignocellulosic energy crops was investigated by simulating a slow pyrolysis process in Aspen Plus [31]. The pyrolysis process generating biochar and heat was compared with direct biomass combustion. The model was used to investigate the effect of biochar on biomass yield and the long-term stability of biochar in the soil. In addition, biochar producing systems demonstrated a significant potential for carbon reduction.

The study on the behaviour of individual biomass components during pyrolysis will not only help in the prediction of slow pyrolysis products yield but also help in the selection of the feedstock. Simulation studies investigating the effect of individual biomass components on the yield of pyrolysis products are limited. Furthermore, the studies on the techno-economic analysis of the slow pyrolysis of individual biomass pseudo-components are also limited. Hence, in this study, the influence of cellulose, hemicellulose and lignin on the yield of char, bio-oil and syngas is investigated using a validated ASPEN Plus model. A detailed techno-economic analysis on the slow pyrolysis of cellulose, hemicellulose and lignin is also carried out using the developed model.

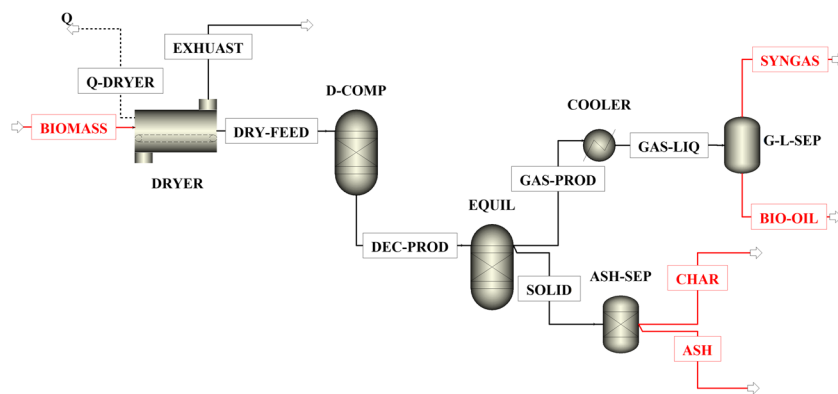
The objective of the study is to investigate the effect of biomass components on the product yields (char, bio-oil and syngas) of slow pyrolysis. The novelty of the work lies in its techno-economic analysis of slow pyrolysis of individual biomass components. The results of the techno-economic analyses of slow pyrolysis of cellulose, hemicellulose and lignin are compared with one another and the best biomass component is identified. The prediction on the yield of slow pyrolysis products will largely be helpful in the selection of the appropriate feedstock for the slow pyrolysis, whereas the cost analysis will be helpful in assessing the optimum economics of the pyrolysis process. In spite of its advantages, the current simulation study has a drawback. The study is based on the assumption that there is no interaction between individual components. However, in a real scenario, i.e. during the pyrolysis of natural biomass, there will definitely be some interactions between the components. Hence, based on this assumption, a slight difference in the slow pyrolysis products yield between the actual experimental results and predicted results is expected.

2 Materials and methods

2.1 Model development basis and assumptions

In this study, Aspen Plus® V9 was selected for the development of a process because the aims of this study are to use advanced simulation techniques to investigate the effect of pseudo-biomass components on the yield of the slow

Fig. 1 Process flowsheet of the pyrolysis system simulated in Aspen Plus



pyrolysis products (char, bio-oil and syngas). Models developed in Aspen Plus software can handle interactions between vapour, liquid and solid phases. Complex systems such as the production of chemicals and oil refineries can be modelled and tested using small sections before being integrated into a connected process. The software provides process engineering with complete integrated solutions. It is supported with large built-in property databanks and additionally has the ability to develop sophisticated unit operations through FORTRAN subroutines [26]. The steady-state simulation of lignocellulosic biomass pyrolysis has been developed in this study under kinetic-free equilibrium basis. The properties of the individual pseudo-biomass components reported by Ma et al. [18] are considered for the current simulation study. In the study, it has been documented that the commercial cellulose powder and xylan (hemicellulose) was procured from Sigma-Aldrich Co., Ltd. (USA), while the lignin was derived from palm kernel shell biomass. The reported properties of the pseudo-components are presented in Table 2.

Table 3 The operating conditions of the pyrolysis model [18]

Analysis	Cellulose	Hemicellulose	Lignin
Feedstock input (kg/h)	1,00,000	1,00,000	1,00,000
Feed T (°C)	25	25	25
Feed P (bar)	1	1	1
Drying T (°C)	150	150	150
Max outlet drying moisture (%)	3.1	3.1	3.1
Pyrolysis T (°C)	450	450	450
Heating rate (°C)	10	10	10
Residence time (min)	30	30	30
Cooling T (°C)	20	20	20
Drying duty (MW)	7.22	6.84	6.17
Pyrolysis duty (MW)	-2.33	-2.55	-47.55
Cooling duty (MW)	-34.59	-34.22	-9.14

The model is simulated on the basis of zero-dimensional blocks, neglecting tar formation, neglecting pressure drops (isobaric operation), neglecting heat losses and assuming a uniform temperature distribution. The zero-dimensional blocks provide the basis of a model system's thermodynamic property. These simulation blocks are assumed to be fully insulated and operating at atmospheric pressure with reaction temperature equals to exit stream temperature. The rest of assumptions are implemented to reduce the complications on the simulated models and support the kinetic-free equilibrium basis.

2.2 Flowsheet and process

The process flowsheet of the Aspen Plus model is presented in Fig. 1. It commences with a dryer block operating at 150 °C primarily to remove any extra moisture content present in the lignocellulosic biomass feedstock. The block reduced the water amount present in the feedstock by specifying the exit stream moisture content. The dried stream entered the decomposition block simulated as a yield reactor in which biomass was converted into conventional components on the basis of the ultimate analysis of biomass using a calculator formulation unit [32, 33]. The streams from the yield reactor were taken to another reactor where chemical composition and phase equilibrium were calculated by minimizing Gibb's free energy at the specified temperature and pressure. The reactor also acted as a two-phase separator, where the gases were separated leaving the top of the reactor and directed to the cooler and the solids (comprises of char and ash) were separated at the base of the reactor. The cooler reduced the temperature and produced a vapour/liquid mixture, which was separated into syngas and bio-oil. Whereas, the solid stream was sent to a solid separator where char was separated from ash fraction.

In order to simulate the real and non-polar species present in the model, the Peng-Robinson equation of state with

Table 4 Economic parameters and relations used by Aspen Plus software

Economic analysis	Relation	Equation number	
Investment cost	(Equipment cost + equipment installation cost + civil, mechanical, electrical and instrumentation cost + administration cost + contingencies)	(1)	
Operation cost	Operating and labour charges + maintenance cost + plant overhead cost + administration cost	(2)	
Annualised cost	Investment Cost $\frac{i(1+i)^n}{(1+i)^n-1}$ + operation cost + raw material cost	(3)	
Operating charges	25% of the shift operating labour cost /period	(4)	
Plant overhead	50% of labour and maintenance cost/period	(5)	
Working capital	5% of investment cost/period	(6)	
Administration cost	8% of total operation costs (operating charges)	(7)	
Salvage value	20% of project capital cost	(8)	
Environmental emissions	Relation	Equation number	
Net stream CO2 equivalents [CO ₂ -e]	(Product streams – feed streams) x GWP	(9)	
Economic parameters	Values	Economic parameters	Values
No. of years (n)	20	Weeks per year	52
Hours per year	8766	Length of start-up	20 weeks
Duration of engineering, procurement and commissioning (EPC)	33 weeks	Duration of construction phase	20 weeks
Depreciation	Straight line	Interest rate (i)	20%/year
Unit cost for supervisor	35/h	Supervisors per shift	1
Unit cost for the operator	20/h	Operators per shift	3
Raw material cost	\$60/ton	Syngas price [37]	\$0.11/m ³
Bio-oil price [38]	\$0.16/l	Biochar price [39]	\$0.2/kg

Boston-Mathias modifications was selected. The model was used to simulate the three pseudo-biomass components: lignin, cellulose and hemicellulose. The operating conditions of the pyrolysis model are presented in Table 3 for the three single component simulation models used to estimate the

characteristics of the pyrolysis process. These operating conditions are selected on the basis of literature study by Kabir et al. [26]. The focus of this study is to analyse the production rates of char, syngas and bio-oil, product yields, moisture and ash effluents and most importantly the economic and environmental performance.

Table 5 The input data and results of the literature and the developed model

	Present model	Visconti et al. [29]
Model conditions		
Feedstock input (kg/h)	50	50
Feed T (°C)	25	25
Feed P (bar)	1	1
Drying T (°C)	500	500
Max outlet drying moist (%)	7.86	7.86
Pyrolysis T (°C)	500	500
Cooling T (°C)	40	40
Results		
Syngas composition (mol. %)		
H ₂	41.2	41.0
CO	4.6	5.0
CO ₂	25.8	26.0
CH ₄	17.1	17.0
H ₂ O	11.1	11.0

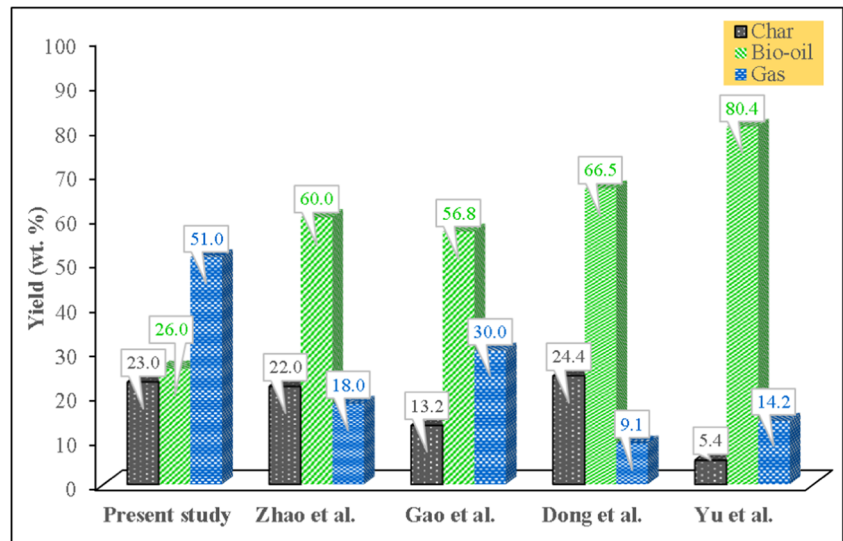
2.3 Techno-economic evaluation

The techno-economic-environmental analysis was conducted by means of the built-in tools of Aspen Plus.

Table 6 The results of the pyrolysis simulation model

Output results	Cellulose	Hemicellulose	Lignin
Char (kg/h)	22,956.10	22,111.51	2636.97
Syngas (kg/h)	50,871.16	52,056.49	38,931.22
Syngas (Nm ³ /h)	108.44	107.65	85.67
Bio-oil (kg/h)	26,172.74	25,832.00	3151.51
Bio-oil (L/h)	26,224.01	25,882.41	3159.48
Moisture (kg/h)	0.00	0.00	0.00
Ash (kg/h)	0.00	0.00	55,280.30
Products yield (%)			
Char	23	22	58
Syngas	51	52	39
Bio-oil	26	26	3

Fig. 2 Effect of cellulose on the slow pyrolysis products yield



The tools were utilised to estimate the investment cost, operation cost, raw materials cost, product sales cost, utilities cost, equipment cost and equipment installation cost. The equations were used in this study to estimate the different costs and environmental emissions presented in our previous studies [34–36] and are summarised in Table 4. Aspen Plus reports the greenhouse gases (GHG) emissions in the form of carbon equivalents of global warming potential (GWP) with respect to data from three popular standards for reporting such emissions. The three standards include the IPCC 2nd Assessment Report on Climate Change from (1995), IPCC 4th Assessment Report on Climate Change from (2007) and the U.S. EPA’s proposed rules from (2009). The emissions are calculated as a weighted sum of the mass flow rates of the GHG components using as weights the 100-year GWP as given by the specified standard. The net stream CO₂ equivalents estimated using Eq. (9) are based on the IPCC 4th standard

[34–36]. The models of the three pseudo-biomass components, cellulose, hemicellulose and lignin, were compared and analysed to study their influence on the yield of char, syngas and bio-oil. The cost and emissions associated with the pyrolysis process were also assured using the model.

3 Results and discussions

3.1 Model result and validation

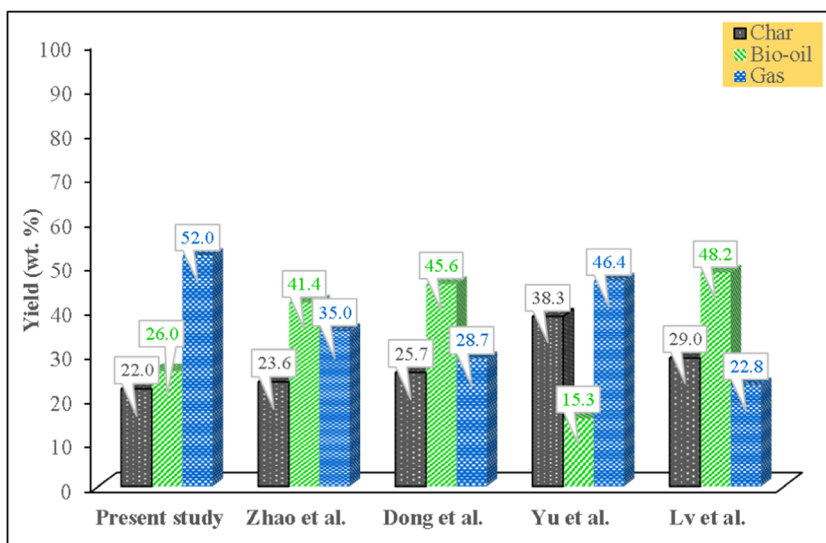
The developed model was validated using the input data reported in the work of Visconti and Miccio et al. and Table 5 presents the input data, the literature results and developed model. The obtained results were compared with the results of Visconti et al. [29]. It can be observed that the obtained results are in perfect agreement with the literature results of the Visconti et al [29].

Table 7 The reported proximate analysis results of cellulose, hemicellulose and lignin in earlier works [8, 40–42]

Biomass components	Earlier works	Proximate analysis			
		Moisture (% wt. basis)	Volatile matter (% wt. basis)	Fixed carbon (% wt. basis)	Ash (% wt. basis)
Cellulose	Zhao et al. [40]	3.31	94.65	2.04	0.00
	Gao et al. [42]	4.54	88.36	7.10	0.00
	Dong et al. [41]	*NR	95.4	*NR	*NR
Hemicellulose	Zhao et al. [40]	3.96	79.42	11.03	5.59
Lignin	Zhao et al. [40]	3.42	67.23	25.50	3.85
	Shafaghat et al. [8]	1.80	62.90	32.60	2.70
	Dong et al. [41]	*NR	*NR	65.05	*NR

*NR, not reported

Fig. 3 Effect of hemicellulose on the slow pyrolysis products yield



The pyrolysis of biomass involves the thermal conversion of the three pseudo-biomass components: lignin, cellulose and hemicellulose into different products that include char, bio-oil and syngas. Studying the effect of each pseudo-biomass component on the product yields would provide a better understanding of the economics of the process. The results of the pyrolysis simulation models are presented in Table 6. From Table 6, it can be observed that a char yield of 58% is obtained from lignin which was 2.4 and 2.5 times higher than cellulose and hemicellulose respectively. On the other hand, the cellulose and hemicellulose showed a higher yield of bio-oil about 26%, which was about 8.67 times more than lignin. The syngas yield was higher for hemicellulose and cellulose about 52% and 51% respectively,

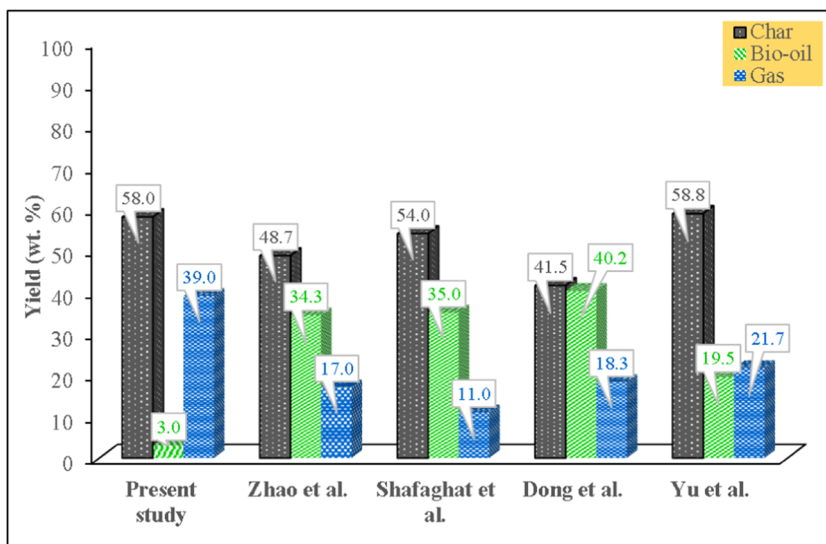
compared to the lignin yield of 39%. It can be noted that the pyrolysis of lignin favoured more char yield while cellulose and hemicellulose favoured more bio-oil and syngas yields.

3.2 Effect of cellulose, hemicellulose, and lignin on slow pyrolysis products

3.2.1 Effect of cellulose on the slow pyrolysis products yield

The effect of cellulose on the yield of char, bio-oil and gas in slow pyrolysis is presented in Fig. 2. Figure 2 also compares the slow pyrolysis product yields of the current work with other works of Zhao et al. [40], Dong et al. [41], Gao et al. [42] and Yu et al. [43].

Fig. 4 Effect of lignin on the slow pyrolysis products yield



In the current work, it can be seen from Fig. 2 that the cellulose delivered significantly more gas yield than char and bio-oil yields. Also, it can be observed that the cellulose produced more bio-oil than char. In the other works (presented in Fig. 2), the cellulose favoured higher bio-oil yield than char and gas yields. However, next to the bio-oil yield, the cellulose did not offer a consistent yield of char and gas. Zhao et al. [40] and Dong et al. [41] observed cellulose favouring the char yield while Gao et al. [42] and Yu et al. [43] reported cellulose favouring the gas yield.

It can be inferred from Fig. 2 that at the given temperature, the cellulose will either favour a bio-oil or gas yield but not a char yield. In general, cellulose does not undergo thermal degradation readily owing to its crystalline structure [44]. However, when it degrades, it undergoes decomposition at a higher rate and the decomposition rate continues until it gets completely degraded (400 °C). This could be the reason for its high bio-oil and gas yield and poor char yield. The reported high yield of bio-oil in the works of Zhao et al. [40], Gao et al. [42], Dong et al. [41] and Yu et al. [43] could be due to the high volatile content of cellulose (see Table 7) [45]. As

observed in the current study, cellulose could also favour the gas yield. Cellulose as such is porous in nature and this porous nature of cellulose allows the vapours formed during pyrolysis to react with solid particles favouring secondary reactions that could lead to more gas generation [46]. The difference in the product yield of cellulose in the above works could be due to the difference in the inherent nature and chemical properties of the cellulose that was used in the respective works.

3.2.2 Effect of hemicellulose on the slow pyrolysis products yield

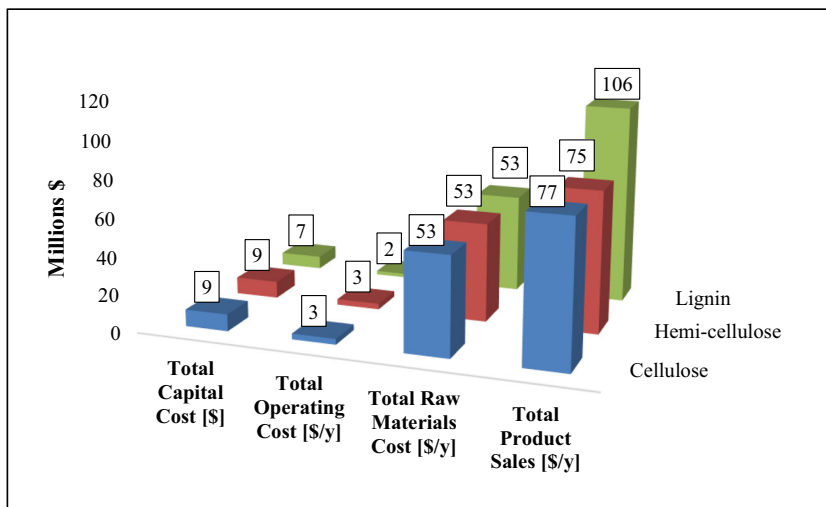
The effect of hemicellulose on the slow pyrolysis products yield is presented in Fig. 3. In Fig. 3, the slow pyrolysis products yields of the current work are also compared with other works of Lv et al. [47], Yu et al. [43], Zhao et al. [40] and Dong et al. [41].

In the current work, it can be noticed from Fig. 3 that the hemicellulose delivered more gas yield than the bio-oil and char yield. Next to gas yield, the hemicellulose delivered more bio-oil yield. Also, it can be observed that the slow pyrolysis

Table 8 Results of the economic and environmental assessment of the model

	Cellulose	Hemicellulose	Lignin
Economics			
Total capital cost (\$)	9.02E+06	9.01E+06	6.96E+06
Total operating cost (\$/year)	3.05E+06	3.03E+06	2.03E+06
Raw material cost (\$/Ton)	60 [53]	60 [54]	60 [52]
Total raw materials cost (\$/year)	5.26E+07	5.26E+07	5.26E+07
Total product sales (\$/year)	7.71E+07	7.51E+07	1.06E+08
Total utilities cost (\$/year) [35]	1.28E+06	1.26E+06	3.65E+05
Equipment cost (\$)	1.87E+06	1.85E+06	1.08E+06
Total installed cost (\$)	3.89E+06	3.88E+06	2.60E+06
Plant life (year)	20		
Rate of return (%)	20		
Total annualised (\$/year)	5.75E+07	5.74E+07	5.60E+07
Product sales (\$/year)			
Bio-oil	3.68E+07	3.63E+07	4.43E+06
Syngas (dry)	1.04E+05	1.04E+05	8.26E+04
Char	4.02E+07	3.87E+07	1.01E+08
Cost per char product (\$/Ton)	285.73	296.55	110.41
Revenue per char product (\$/Ton)	383.30	387.82	208.89
Net profit per char product (\$/Ton)	97.57	91.27	98.49
Cost per bio-oil product (\$/Ton)	250.61	253.84	2029.00
Revenue per bio-oil product (\$/Ton)	336.19	331.97	3838.92
Net profit per bio-oil product (\$/Ton)	85.58	78.12	1809.93
Cost per syngas product (\$/Ton)	128.94	125.96	164.25
Revenue per syngas product (\$/Ton)	172.97	164.73	310.76
Net profit per syngas product (\$/Ton)	44.03	38.77	146.51
Net CO ₂ emissions (kg CO ₂ -e/h)	235,210.46	223,945.48	56,876.24

Fig. 5 Production cost and revenue for the three pseudo-biomass components



products yield of hemicellulose is similar to the slow pyrolysis products yield of cellulose. In the other works (presented in Fig. 3), the hemicellulose mostly favoured the bio-oil yield than char and gas yields. Next to bio-oil yield, the hemicellulose mostly supported the gas yield. It can be inferred that at 450 °C, the hemicellulose will either favour the bio-oil or gas yield. This could be attributed to the thermal decomposition behaviour of hemicellulose [23]. As hemicellulose is mainly composed of amorphous structured saccharides, it readily undergoes degradation even at low temperatures. In fact, decomposes completely even before reaching 400 °C. The high yield of bio-oil and gas could also be due to the high volatile content of hemicellulose [25] as can be seen in Table 7. Conversely, the low yield of char could be attributed to its low ash content as presented in Table 7 [48]. The discrepancy in the product yield of hemicellulose in the above works could be due to the difference in the physical and chemical characteristics of hemicellulose.

3.2.3 Effect of lignin on the slow pyrolysis products yield

The influence of lignin on the yield of char, bio-oil and gas in slow pyrolysis is presented in Fig. 4. Figure 4 also compares the slow pyrolysis products yields of the current work with other works of Shafaghat et al. [8], Yu et al. [43], Zhao et al. [40] and Dong et al. [41].

Table 9 Comparison of product costs with literature

Product	Cost			
	Cellulose	Hemicellulose	Lignin	Literature
Char (\$/kg)	0.29	0.30	0.11	0.2 [39]
Bio-oil (\$/L)	0.25	0.25	2.02	0.16 [38]
Syngas (\$/m ³)	0.31	0.32	0.29	0.11 [37]

In the present work, lignin yielded more char 58% than bio-oil and gas yield. Second to the char yield, the lignin delivered more gas than bio-oil. In the other works (presented in Fig. 4), the lignin also favoured the highest char yield over bio-oil and gas yields. However, for the second highest yield after char, the lignin did not offer a consistent trend in the yields of bio-oil and gas. In the works of Zhao et al. [40], Shafaghat et al. [8] and Dong et al. [41], a relatively a higher yield of bio-oil was reported while in the work of Yu et al. [43], a higher yield of gas was observed. The high char yield of lignin could be attributed to the incomplete decomposition of lignin, since lignin is constituted of complex molecules, which undergo degradation at a wider temperature range, i.e. 160–900 °C. At the given temperature of 450 °C, lignin could not have undergone complete decomposition; hence, a high char yield is obtained [49]. The high fixed carbon of lignin could also have been contributed to the high char yield as presented in Table 7 [50]. Also, the presence of ash could have promoted the char yield as the inorganic elements in the ash acts as catalysts leading to more char formation as represented in Table 7 [51]. The variation in the product yields of lignin in the above works could be because of the difference in their physical and chemical properties.

3.3 Techno-economic and environment evaluation

The evaluation of the specific economic profitability for the three pseudo-biomass components is essential to study the influence on the overall viability of the pyrolysis process. In addition, coupling the economic evaluation with environmental impact assessment strengthens the comparison study and enhances the dual objective assessment. The results of the economic and environmental evaluation of the model are presented in Table 8. The four main economic indicators namely product sales and the costs of capital, operating and raw materials are presented in Fig. 5 and it can be seen that raw

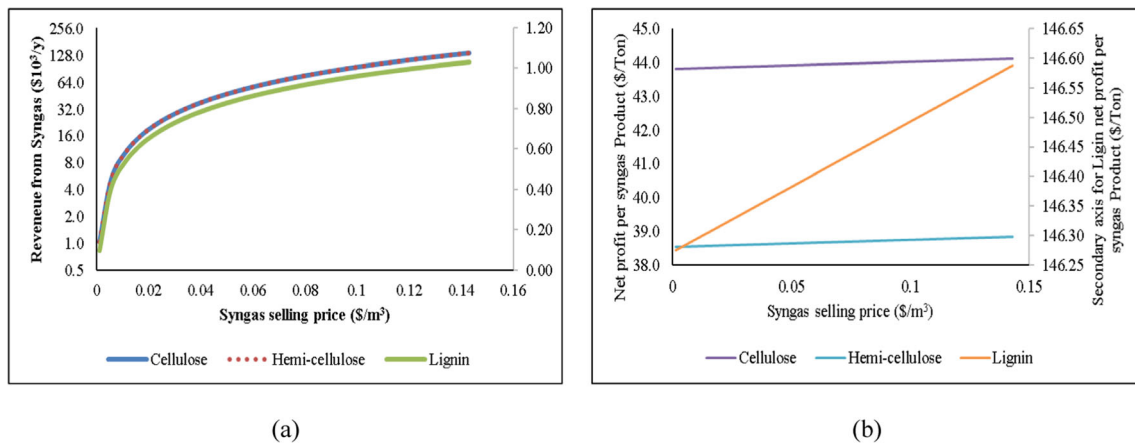


Fig. 6 Sensitivity trend of syngas. **a** Revenue and **b** net profit per syngas product against changes in the selling price

materials cost is the largest contributor to the overall cost. This high cost is originated from the high feedstock cost reported in literature [52]. By comparing and analysing the annualised cost against the generation rates of the different products indicates that the hemicellulose-based pyrolysis gives the highest positive net profit per char product. In particular, the production costs for char are 110.4 \$, 285.7 \$ and 296.5 \$ per ton using lignin, cellulose and hemicellulose respectively. Whereas, the revenues from char production demonstrate positive net profit for all pyrolysis cases with approximately 98.49, 91.27 and 97.57 \$ per ton of char produced using lignin, cellulose and hemicellulose respectively. The net profit from the production of bio-oil and syngas has also supported the economic feasibility of the pyrolysis process. The net CO₂ emissions expressed as kilogram of CO₂-e per hour indicate that lignin-based pyrolysis emits the lowest quantity of CO₂ environmental emissions.

The results of product costs demonstrate good agreement with literature values as illustrated in Table 9. The reported product cost for biochar in literature ranged between \$0.2 and 0.8/kg which demonstrates good agreement with the current study value estimated in the range of \$0.1–0.3/kg. In addition, the product costs of bio-oil and syngas from the current study

estimated at \$0.3/m³ and \$0.25/L are in the range of reported literature values. The case for Lignin pyrolysis has reported some deviation from the reported literature values which can be due to the high char yield compared to the other two studies.

In an effort to assess the potential variation in the prices of the different products generated from the slow pyrolysis process, this study further evaluates the effect on the revenue and net profit. The prices of the products are varied from 1% of the original price to 30% above the original price. Figures 6, 7 and 8 illustrate the trends of resulted revenue and net profit for the different biomass components as a function of the product's prices. The sensitivity trends of the revenue and net profit from the different products demonstrate strong behaviour for syngas results compared to char and bio-oil. Decreasing the price to 1% of the original reported literature value for the three products show no negative results for the net profit per syngas product while the trends for bio-oil and char products indicate a breakpoint in the net profit approximately at 0.88 \$/L and 0.11 \$/kg, respectively. Among the different components, lignin was found the most to resist the change in the selling price of the different products. The revenue from the different products demonstrates sharp increase at small selling

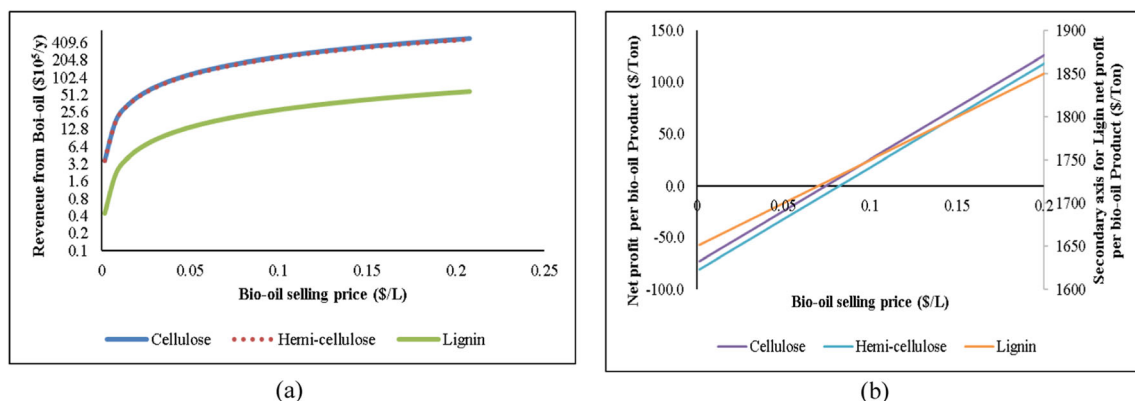


Fig. 7 Sensitivity trend of bio-oil. **a** Revenue and **b** net profit per bio-oil product against changes in the selling price

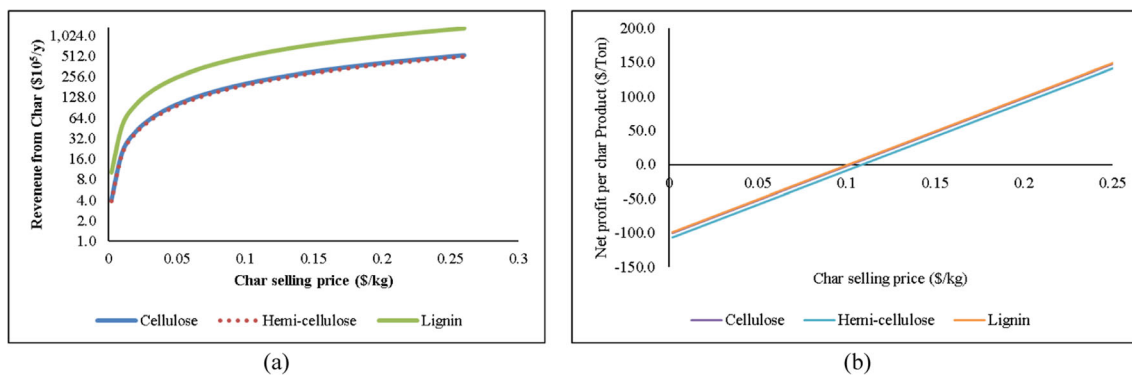


Fig. 8 Sensitivity trend of char. **a** Revenue and **b** net profit per char product against changes in the selling price

prices between \$0–0.02/m³, \$0–0.05/L and \$0–0.05/kg for syngas, bio-oil and char, respectively. Whereas, increasing the selling prices prove to flatten the revenue trend. Similar to the previous observations, the revenues from syngas and bio-oil are more for cellulose and hemi-cellulose, while the revenue from char is more for lignin.

4 Conclusion

This study investigated the effect of biomass components (cellulose, hemicellulose and lignin) on pyrolysis product yields such as bio-oil, char and syngas using an ASPEN Plus-based model. The simulation study was performed at a pyrolysis temperature of 450 °C, a heating rate of 10 °C/min and a solid residence time of 30 min. The simulation results indicated that at the given conditions, the lignin contributed 2.4 and 2.5 times more char yield than cellulose and hemicellulose respectively. The hemicellulose, on the other hand, contributed 1.33 times more syngas yield than lignin while the cellulose and hemicellulose contributed 8.67 times more bio-oil yield than lignin. It can be inferred that lignin favours char yield while cellulose and hemicellulose favour bio-oil yield. The techno-economic analysis indicated that the cost involved in the production of char using lignin (110 \$/ton) was significantly lower than using cellulose (285 \$/ton) and hemicellulose (296 \$/ton). The net CO₂ emission of lignin pyrolysis was 4.14 times lower than cellulose pyrolysis and 4.15 times lower than hemicellulose pyrolysis. It can be concluded that lignin pyrolysis is more advantageous than cellulose and hemicellulose pyrolysis. In the selection of feedstock for the slow pyrolysis, feedstock with more lignin should be always preferred. The present study is based on the assumption that there is no interaction between individual components during pyrolysis. However, in a real case, there will definitely be some interactions between the components of biomass. Hence, future studies should develop a model considering individual as well as synergistic effects of the biomass components.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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