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THE STUDY OF LIGNOCELLULOSIC BIOMASS PYROLYSIS VIA SUPERPRO DESIGNER

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ABSTRACT

The renewable energy industry is widely utilizing biomass as one of the extraction sources. Pyrolysis is among the most commonly used technique to process biomass into desired fuels. Biomass mainly consist of cellulose, hemicellulose and lignin that will decompose differently during pyrolysis yielding valuable bio-oil, bio-gas and bio-char. Traditional experimental work to study biomass pyrolysis could be complex and time consuming. This study has utilized SuperPro Designer (SPD) as a modelling tool to investigate the pyrolytic behavior of biomass constituents and product distributions. The model was built based on kinetic studies of lignocellulosic reaction pathways. The obtained results were verified with experimental as well as literature data. The flexibility and accuracy of SPD model were also tested with different biomass species. The model was validated and can be used as a predictive and optimization tool for the study of biomass pyrolysis.

Keywords: renewable energy sources, biomass, pyrolysis, kinetics, mathematical modelling

NONMENCLATURE

Abbreviations	
CSTR	Continuous Stirred Flow Reactor
PFR	Plug Flow Reactor
SPD	SuperPro Designer

1. INTRODUCTION

World energy consumption is experiencing an exponential growth and is expected to increase up to 815 quadrillion British Thermal Unit in 2040 [1]. The United States Energy Information Administration reports that rapid economic growth in Asia, particularly in countries such as India and China will be accounted for 60% of global energy consumption [2]. Petroleum-based liquid fuels are the largest source of energy used across the globe. As oil prices increase since 2016, various energy consumers are turning to a more economical-feasible alternative sources. Among them, renewable sources is anticipated to be one of the fastest growing industry in between year 2015 to 2040 with an average 2.3% increase in annual consumption [2]. China alone has recorded a 42 billion kWh of energy usage generated by renewable sources in 2013 [3].

Biomass is a renewable energy source from organic matter that has stored energy form the sun. Primary sources of biomass for energy generation include wood, agricultural remains, food waste and animal manure [4]. Biomass is made up of organic matrixes consisting carbohydrates and aromatic compound polymers known as the lignocellulosic components. Lignocellulosic biomass is composed mainly of cellulose, hemicellulose, lignin and minor minerals content [5]. Cellulose binds glucose units, hemicellulose provide structural strength to cell walls while lignin contributes to cell wall stiffness and strength of individual fibres. The general distribution of cellulose, hemicellulose and lignin in biomass is found to be 35 – 50%, 20 – 35% and 10 – 25% respectively [5].

Among commercialized technologies for biomass energy extraction, pyrolysis is one of the oldest methods in existence. Pyrolysis is the thermal degradation of biomass components at high temperature with the absence of oxygen, releasing valuable char, oil and gas for energy generation. Many studies have explored the operating conditions in relation to product yield. A dense fluidized bed reactor is optimized to 500°C for a complete decomposition of biomass to yield maximum oil production [6]. Biomass degradation studies found that hemicellulose will degrade first at 250°C, followed by cellulose at 300°C and finally lignin at 400°C [7]. These complex and prolonged experimental work could be simplified by approaching the use of mathematical simulation tools to study and investigate process behaviours.

2. METHODOLOGY

2.1 Experimental set up

Hardwood birch and softwood pine samples were pyrolyzed in a tube furnace to study the behavior of biomass pyrolysis. Raw samples were first grinded in a centrifugal mill for particle size reduction to 200 - 250 µm. Drying took place at 105°C for 24 hours for moisture removal. The pyrolysis temperature was set at 550°C with a heating rate of 10°C/min under constant nitrogen flowrate of 100ml/min. A condenser and gas bag connected to the system outlet was used to collect volatiles and light gases for yield calculation.

2.2 Kinetic model

Biomass pyrolysis is generally described in three stages: (1) dehydration, (2) primary decomposition and (3) secondary cracking. Most existing studies are based on the Ranzi's model [8] where cellulose will first form an intermediate known as active cellulose and levoglucosan before successive radial reaction in polymer chain forms secondary tar and gas. Hemicellulose pyrolysis is approximated by xylose monomer where intermediates will be formed first, followed by the release of gaseous products at higher temperature. As for lignin, its complex polymers derived from hydroxycinnamyl alcohol monomers are difficult to examine its characteristics in pyrolysis. Reference components rich in carbon, hydrogen and oxygen were used to study the intermediate and progressive charification of solid residues.

The simplified black box model for cellulose pyrolysis proposed by Ranzi was integrated with a more complete conversion path. To obtain an in depth cellulose kinetic model, a multistep reaction pathway collected from different sources [9, 10] was generated and used in SPD simulations. The initial four reactions were enhanced to seven first order reactions together with two refined char forming mechanism. The reaction pathway of biomass lignocellulosic components are illustrated in Figure 1. Each individual degradation pathway were represented as chemical equations and used as basis to set up the pyrolytic reactors in SPD model.

2.3 Modelling tool

SuperPro Designer (SPD) is a modelling tool for the evaluation and optimization of integrated process widely applicable in biotechnology, food, chemicals and processing industries. SPD has coupled manufacturing and environmental operation models into the package allowing user to predict future behavior of a process, quantifying mass and energy balances as well as calculating reactions and kinetics of complex systems.

By utilizing SPD, individual performance of cellulose, hemicellulose and lignin will be simulated with known flowrates to estimate its product yields. The reaction takes place under similar conditions as the experimetal setup where biomass will be pyrolyzed at 550°C in a non-oxidative atmosphere. The two stages in pyrolysis is represented by a continuous stirred-flow reactor (CSTR) and a plug flow reactor (PFR) in SPD where CSTR represent the primary decomposition of biomass while PFR indicated the secondary reactions for pyrolysis. A general flow diagram of the pyrolysis model is illustrated in Figure 2.

Table 1: Lignocellulosic component split for birch and pine wood

Biomass	*Cellulose (wt%)*	*Hemicellulose (wt%)*	*Lignin (wt%)*
Birch[11]	40	39	21
Pine[11]	40	28.5	27.7

Due to the limitations in current physical analysis technology, detailed product distribution of cellulose, hemicellulose and lignin could not be identified. Hence the SPD model used is not characterizing biomass structures or interactions between products in the secondary reaction. Uniform heating is also assumed for the model to avoid complications in heat transfer considerations.

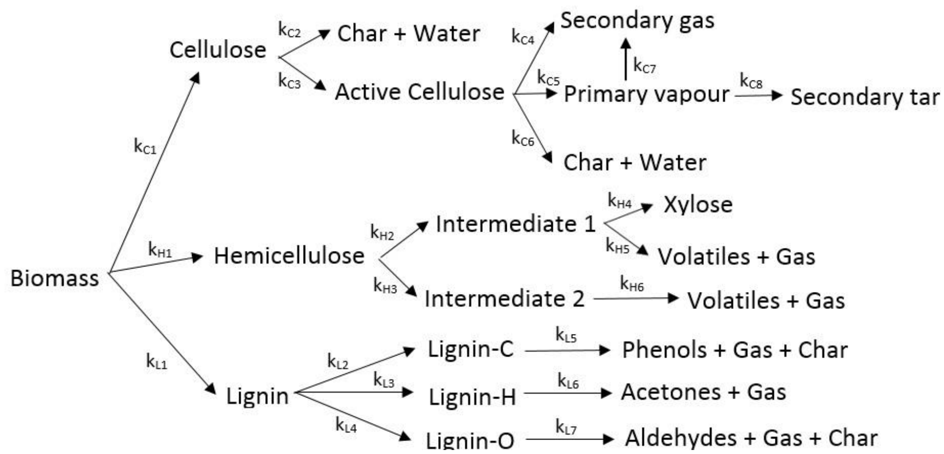

Figure 1: General reaction pathway of biomass pyrolysis.

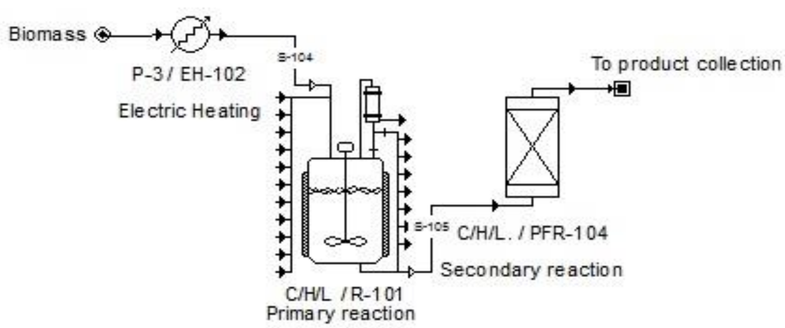

Figure 2: Process Flow Diagram of biomass pyrolysis in SPD.

3. RESULTS AND DISCUSSION

3.1 Model validation

Pyrolysis of birch and pine wood are carried out in laboratory to obtain experimental results for model verification. The operating conditions for SPD are set to be identical to the experiment and literature data of same biomass at similar operating conditions are also utilized to reaffirm the outcome for both cases. The yield of solid, liquid and gas product of three cases are listed in Table 2.

Table 2: Product yields of biomass from experiment (Exp), SPD and literature reference (Ref).

	Birch wood (wt%)			*Pine wood (wt%)*		
	Exp	SPD	Ref[12]	Exp	SPD	Ref[13]
Char	29.64	25.75	27.00	29.65	29.33	27.20
Oil	37.08	39.70	43.00	35.71	42.59	41.50
Gas	32.27	34.54	30.00	34.62	28.07	31.30

The collected data are converted into Figure 3 and 4 for clearer illustration of the product distributions. From the plotted graphs, both biomass type exhibit clear trend of having highest bio-oil yield followed by bio-gas and bio-char (the distribution trend will be discussed in section 3.2) regardless in experimental, simulated or collected reference data. From calculations, the overall percentage error for experimental results to literature value is <13% while for SPD the error is approximated to <10%. Thus, it can be said that the model used in SPD is capable of producing results that reflects actual biomass pyrolysis.

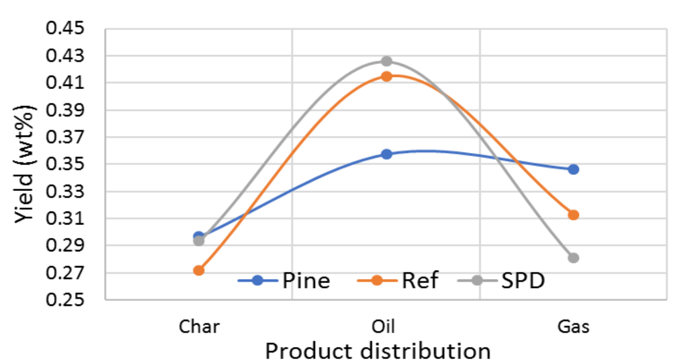

Figure 1: Product yield and distribution of pine wood.

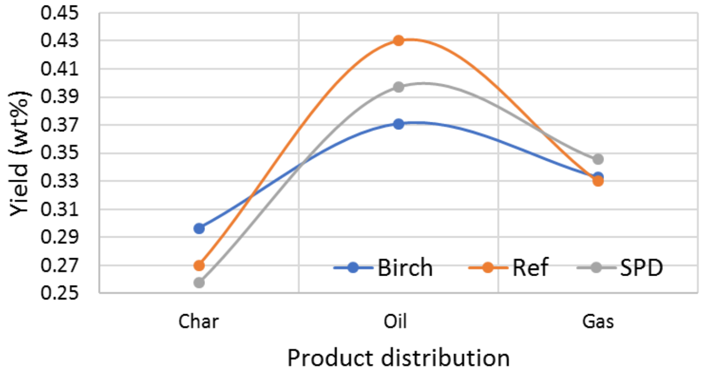

Figure 2: Product yield and distribution of birch wood.

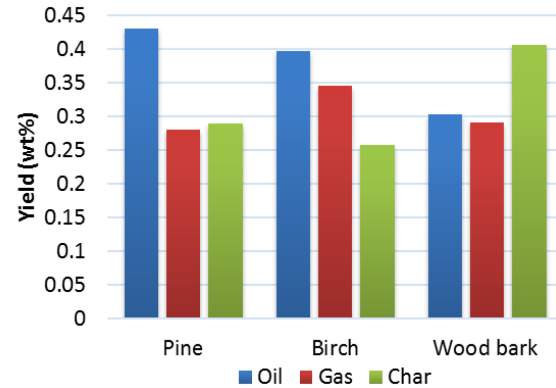

Figure 3: Pyrolysis yields predicted by SPD.

3.2 SuperPro Designer for product yields prediction

As cellulose, hemicellulose and lignin has relatively different formulas and structures, the decomposition mechanism during pyrolysis for product release is also different. Cellulose, having glycosidic bonds will be highly reactive above 300°C. The depolymerized intermediates will be rapidly converted into volatile components where majority of them are condensable organic compounds. Furans which are important components in bio-oil will be obtained upon the completion of degradation . The unstable polysaccharide chains in hemicellulose will undergo depolymerization after 240°C yielding significant amount of water and pyrolysis gas . As for lignin, the benzene and aromatic rings in its structure will release primary volatiles at 200 to 450°C. Then, the rearrangement of aromatic structures contribute to high char formations .

The SPD model is further tested for flexibility and accuracy by inputting biomass with different cellulose, hemicellulose and lignin composition to predict its product yields. Both pine and birch wood are cellulose-rich biomass while wood bark has higher lignin content in its composition. To highlight, birch wood has the highest hemicellulose split among all samples. From the results simulated from SPD, it could be observed that pine and birch wood produced high percentage of bio-oil while wood bark gives mainly solid char products. High content of hemicellulose in birch wood has also reflected highest gas yield in the simulation.

It is shown that SPD has generated results relevant and of equal as per literature suggests that high cellulose content produces higher bio-oil while hemicellulose gives gas and lignin yield highest char. The model built is hence proven to be reliable and could reflect the actual pyrolysis condition which will be useful to study the performance of different biomass in pyrolysis under different operating conditions.

4. CONCLUSION

A SuperPro Designer (SPD) model was built based on an integrated kinetic reaction pathways of cellulose, hemicellulose and lignin to study the performance of different biomass during pyrolysis reactions. The simulated results were verified with experimental as well as literature values and the percentage differences are within 10%. The model was then further tested for its flexibility with different biomass with varying lignocellulosic compositions. The model has successfully predicted biomass with high cellulose, hemicellulose and lignin contents will yield high bio-oil, bio-gas and bio-char, respectively. The proposed SPD model is an effective, accurate and efficient approach to study pyrolysis and has potential for wider applications.

5. ACKNOWLEDGEMENT

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