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Process Modelling and Simulation of Fast Pyrolysis Plant of Lignocellulosic Biomass Using Improved Chemical Kinetics in Aspen Plus®

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The successful operation of biomass pyrolysis plant on an industrial scale would showcase and promote the possibility of practical decarbonizing energy projects. This work presents a comprehensive Aspen Plus® modeling work of fast pyrolysis processes for lignocellulosic biomass based on kinetic reaction mechanisms. The simulation uses mass and energy balance calculations to forecast the product yields and composition depending on different sets of operating conditions (temperature, residence time) and feedstock composition includes conventional components, nonconventional components, and solids component of lignocellulosic biomass. The reaction kinetic models are developed from the principle of biomass pyrolysis using data available from the literature. The product yield from a biomass pyrolysis pilot plant is used to demonstrate the validation of the model. The results show a high correlation of the results for both slow and fast pyrolysis processes compared with those from the pilot plant and the previous works. The simulation model is found to be able to correctly predict fast pyrolysis products' yields within the typical range of operation considered (high reaction temperatures with low residence times). In conclusion, the model proved to be suitable for predicting fast pyrolysis reactions for lignocellulosic biomass feedstock and can be used for estimating the trend of pyrolysis products without the need for experimental data with t-test of differential of product yield's trend at 95 % confidence interval as 0.00327. This fast pyrolysis model offers rapid assessment for energy projects associated with the transition towards low-carbon development in Asia.

1. Introduction

Biomass is an obvious renewable energy resource to sustain national energy needs. In many countries, a large amount of agricultural waste after harvesting could be used as biomass energy. Pyrolysis process is considered as an effective conversion technology due to the products generated and the energy recovery (Oyedun et al., 2012), which is carried out in the absence of oxygen at intermediate to high temperatures (500–650 °C), low residence times (< 2–3 s) and high heating rates (> 1,000 °C/s) (Bridgwater, 2012).

The successful operation of biomass pyrolysis plant on an industrial scale would promote the possibility of practical decarbonizing energy projects (Jaroenkhasemmeesuk et al., 2018). The drawback of biomass promoted as alternative energy is variety and differences of raw materials in pyrolysis that require different controlled operation parameters; material moisture, temperature, etc. To reduce the experimental cost, process modeling is a significant tool for investigating process performance and analyzing the impact of operation parameters. The simulation of biomass pyrolysis plant has been developed for many recent years to reduce the cost of the optimization process in the actual plant. Simulation program from Aspen Technology Inc. is the chemical process optimization software, used to design, simulate, predict and optimize the performance of pyrolysis plants. Aspen Plus® can estimate the yield and composition of the fast pyrolysis products depending on reactor conditions and feedstock composition without the need for experimental data as input. The heat and mass balances of the process are the main algorithm in Aspen Plus®.

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Most of the modeling works have focused on the overall efficiency of the pyrolysis plant, with a variety of reactor models. A pyrolysis reactor in Aspen Plus® model in previous works can be categorized into two types of reactor models; Gibbs reactor (RGibbs), and Yield reactor (RYield). Both RGibbs and RYield are used when the reaction kinetics and stoichiometry are unknown (Aspen Technology Inc.,2013). RGibbs solves its model by minimizing Gibbs free, while RYield performs the calculations based on the yield that was specified in the model. They claimed that this model used more than 100 equations to increase reliability. Onarheim et al. (2015) used an RYield reactor block for simulating the fast pyrolysis model claimed that the reaction mechanisms for fast pyrolysis of wood are poorly understood. The result showed that this model would be accompanied by a certain degree of unreliability. The mentioned models are based on a range of sources accumulated into one composite compilation. Various sources collection leads to a significant risk of unrealistic model analysis because the collected data from various process conditions such as feedstock types may diverge.

Small-scale modeling can be analysed as the mentioned model. But large-scale continuous units may require a higher reliable validation of a simulation model, as these generate more reliable data when processes are scaled up to demonstration or commercial size. When rigorous simulation of reactors is needed, the RCSTR will be used. CSTR reactor will approach a more realistic description of the process. Peters et al. (2014a) used RCSTR together with Ryield to model the fast pyrolysis plant. The result showed higher reliability of yield than other models and be able to significantly improve the efficiency of the overall plant to 73.2 %. This work aims to present a comprehensive Aspen Plus® modeling work of fast pyrolysis processes for lignocellulosic biomass based on only main kinetic reaction mechanisms from Pelucchi et al. (2018), of pyrolysis process of lignocellulosic biomass. The expected result of this work should be able to represent more reliable of pyrolysis product yield and simpler to operate or to remodel than previous works.

2. Modeling of lignocellulosic biomass pyrolysis plant

Aspen Plus® can be used to model processes involving solids and can complete integrated solutions for process engineering including reactor as well. The heat and mass balances of the process are the main algorithm in Aspen Plus®. Moreover, RCSTR needs more technical detail in design variables (pressure and temperature or heat duty), specification of the valid phases, and a reactor specification (residence time). The results from the simulation of the Gibbs reactor is based on calculations where the reactions reach thermodynamically and chemical equilibrium over an infinity of time (Aspen Technology Inc., 2013). In a real pyrolysis process, the time of reactions should be considered as finite, and the different reactions have different reaction rates.

2.1 Feedstock specification

In this work, three types of components were used includes conventional components, nonconventional components, and solids component based on ultimate and proximate analyses shown in Table 1. Normal components were identified as conventional components. Other solid component includes sawdust component, biochar, and ash will be identified as nonconventional and solid components. Sawdust, char, and sand played significant roles in the model as a nonconventional solid component

Table 1: Ultimate and proximate analyses of the feedstocks

Reference	This work	Ward et al. (2014)
Air-dried moisture (%)	7.68	6.1
Ash (%)	2.5	1.0
Volatile matter (%)	73.65	77.6
Fixed carbon (%)	16.18	15.3
Gross calorific value (%)	-	18.12
Carbon (C) (wt%)	45.0	47.2
Hydrogen (H) (wt%)	6.71	5.66
Oxygen (O) (wt%)	24.23	45.91
Nitrogen (N) (wt%)	0.16	0.2
Total sulphur (S) (w%)	0.02	0.03
High heating value (HHV) (MJ/kg)	16.37	18.11

In addition to specialized physical property models for solid components, accurate representation of the solids particle size distribution is required for processes. Sawdust as the raw material in this work was modelled in the simulation as a nonconventional solid component in feedstock using the proximate and ultimate component attributes.

2.2 Chemical kinetics of pyrolysis

The reaction mechanism is based primarily on the works of Corbetta et al. (2013), and Calonaci et al. (2010), together with the kinetic mechanism and model validation from Pelucchi (2018). A mechanistic kinetic model of biomass pyrolysis was developed at the particle scale in order to describe the relative role of reaction kinetics and transport resistances. Kinetic models of the different steps of solid fuel volatilization include CELL, HCE and LIG were developed and validated together with secondary gas-phase reactions through then compared with experimental data. To promote the simple expressions, these models allow the characterization of the degradation steps, their characteristic times, and the prediction of product distributions, as shown in Table 2. It implements 15 individual reactions, including primary and secondary decompositions.

Table 2: Developed pyrolysis reactions

Reaction	Kinetic constant (1/s)	Activation energies (kJ/mol)
CELL -> CELLA	8.00E+13	192.5
CELL -> 5H_2O + 6Char	8.00E+07	125.5
CELLA -> LVG	4T	41.8
CELLA -> 0.95HAA + 0.25Glyoxal + 0.2Aceta +0.25HMFU + 0.2Aceton + 0.16CO_2	1.00E+09	133.9
HCE -> 0.4HCE1 + 0.6HCE2	1.00E+10	129.7
HCE1 -> 2.5H_2 + 0.124H_2O + CO + CO2 + 0.25Methanol + 0.5Formaldehyde + 0.125Ethanol +2Char	3.00E+09	113
HCE1 -> Xylan	3T	46
HCE2 -> CO_2 + 0.5 CH_4 + 0.25C_2H_4 +0.8CO + 0.8H_2 +0.7Formaldehyde + 0.25Methanol + 0.125Ethanol +0.125H_2O + Char	1.00E+10	138.1
LIG-C -> 0.35LIG_{CC} + 0.1pCoumaryl +0.08Phenol + 0.41C_2H_4 + H_2O + 0.495CH_4	4.00E+15	202.9
LIG-H -> LIG_{OH} + Aceton	2.00E+13	156.9
LIG-O -> LIG_{OH} + CO_2	1.00E+09	106.7
LIG_{CC} -> 0.3pCoumaryl + 0.2Phenol +0.35Acrylic + 0.7H_2O + 0.65CH_4 + 0.6C_2H_4 + 1.8CO + H_2 + 6.4Char	5.00E+06	131.8
LIG_{OH} -> LIG + H_2O + Methanol + 0.45CH_4 + 0.2C_2H_4 + 2CO + 0.7H_2 + 4.15Char	3.00E+08	125.5
LIG -> Lumped-phenol	8T	50.2
LIG -> H_2O + 2CO +0.2Aceton + 0.4Methanal + 0.2Aceta + 0.2Formaldehyde + 0.6CH_4 + 0.65C_2H_4 + 0.5H_2 + 5.5Char	1.20E+09	125.5

In this model, char was assumed as consisting of 100 % carbon to make chemical kinetics of fast pyrolysis elemental equilibrium. In previous work such as Jindo et al. (2014), biochar from wood-based fast pyrolysis consisted of 77.5-84.8 % carbon. In the future, to adjust the accuracy of compositions of biochar, Ryield may be provided to change carbon composition in this model to oxygen, hydrogen and nitrogen.

Calonaci et al. (2010) used a comprehensive kinetic model of biomass pyrolysis in the fast pyrolysis model. The results clearly showed and quantified the critical role of heat-transfer and secondary pyrolysis reactions in bio-oil yields from fast pyrolysis of biomass. The comprehensive kinetic model correctly predicted the relative amount of char, liquid, and gas fractions and also gave useful design and optimization-related information. The char fraction was modelled by balancing the chemical kinetics of pyrolysis. In this lignocellulosic biomass pyrolysis, the kinetics model adopted 100 % carbon.

The pyrolysis reactor requires a certain amount of heat provided by sand circulating in combustor which burns the pyrolysis gases and part of the char. In previous work of Peters et al. (2014b) hot sand was not circulated through between the combustor and the pyrolysis reactor but circulated and heat transferred. Char and non-condensable gases which separated from the pyrolysis reactor will move to the followed combustor to generate the simple combustion reactions using an RStoic reactor. The heat generated in this combustion was also considered to be used as a heat source in the dryer process to dehydrate pyrolysis feedstock and to reheat the sand to the fast pyrolysis reactor.

Process simulation in this work was modelled from the flow process of a fast pyrolysis pilot plant in Thailand. Simulation flowsheet of the biomass pyrolysis process in this work was shown in Figure 1. Biomass will be passed to the dryer to eliminate moisture. This process is not affected directly to the pyrolysis process but to fulfill the process based on the pilot plant. After moisture removing biomass will move to Ryield to change solid component into conventional components, nonconventional components, and solids component of lignocellulosic biomass which can be processed in the pyrolysis reactor. In the pyrolysis reactor the reaction mechanism as shown in Table 2 will be operated based on the relation between kinetic constant, activation energies and operation parameter. After a fast pyrolysis process, bio-oil, as the products, is cooled and collected. The detail of each operation part is described in Table 3.

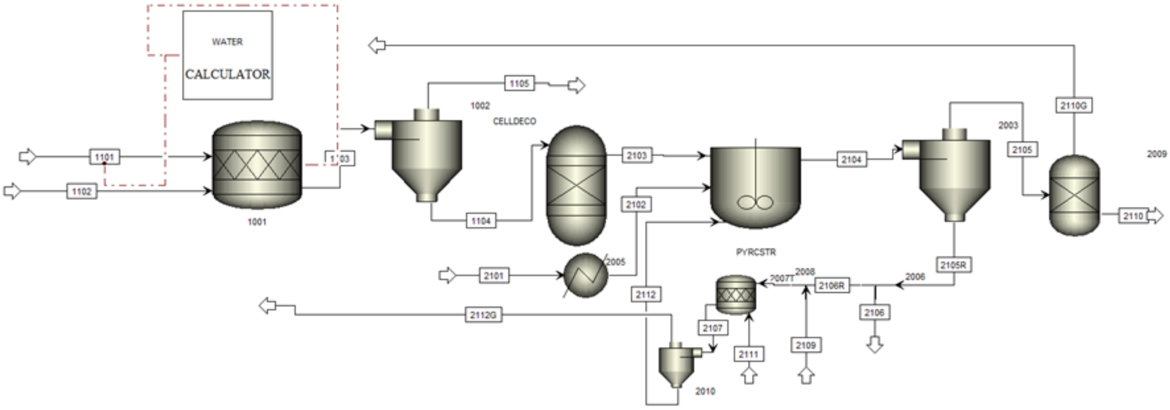

Figure 1: Simulation flowsheet of the biomass pyrolysis process implemented in Aspen Plus®

Table 3: Description of Aspen block operation

Block	ASPEN Block ID	Operation
DRYER	RSTOIC	Removing moisture to 7% before combustion
DECOMP	RYIELD	Decomposition of feedstock (Sawdust) into components for reaction (components and energy output)
PYROLYSIS	RSTOIC	Operating pyrolysis reactor with developed pyrolysis kinetic reactions
CYCLONE	CYCLONE	Solids Separation
HEATER	HEATER	Simulating the temperature of the unreacted carbon to the reactor temperature.
SEPARATOR	COOLER	Dividing products in a separator (FLASH2) to gases and liquid

3. Results and discussion

The product yields from the pyrolysis model were analysed based on temperature and residence times. Moreover, bio-oil yield in the fast pyrolysis model was compared with the results from previous works on a laboratory scale and pilot in the same aim as fast pyrolysis.

3.1 Residence time and temperature dependency

The dependency of the product yields on temperature and residence time was simulated and investigated. The results of the simulation runs are presented in Figure 2 to compare between the simulation result and result from the pilot plant. Figure 2a shows the product yield from simulation includes water, solid, gas, and oil product while the result from the experiment was shown in Figure 2b. The yield curves show the typical shape for pyrolysis reactions, with the maximum liquid yield about 50% at around 550 ºC and residence times of 1 s. This condition was considered as fast pyrolysis. The liquid products' yield increased sharply when the temperature increased. According to pilot plant data (Jaroenkhasemmeesuk and Tippayawong, 2016), at the fast pyrolysis condition 1-2 s of residence times, this model gave the reliable result of the product yields of fast pyrolysis at intermediate to high temperatures (500–600 °C).

The trend of product yields from the simulation was compared with the result from the experiment using the differential of their trend curve. T-test at 95 % confidence interval was investigated, and the t-value of these two results is 0.00327 maximum. It may conclude that the trend of product yield between simulation and the experiment was not significantly different.

The highest difference percentage of product yields between simulation and experiment was at 450 °C of reaction temperature as shown in Figure 2a and 2b. The solid product from the experiment was about 69 %

while the simulation showed only 50 %, while the oil product yield from the experiment was lower than simulation about two times. This may explain that, at 450 °C reaction temperature, the experiment cannot satisfy low residence time condition.

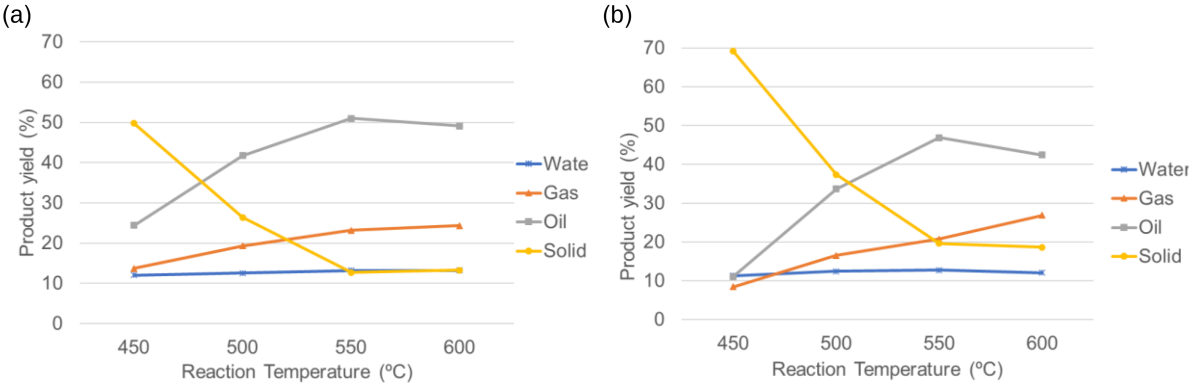

Figure 2: *Comparison of liquid product yield of fast pyrolysis between (a) simulation and (b) previous works in pilot plant*.

3.2 Bio-oil components

Figure 3 shows that the temperature at the peak of the bio-oil yield (550 °C) was slightly higher than the typical ranges of 500–520 °C for wood biomass from the literature review and experiments (Salehi et al., 2013; Heo et al., 2010). This literature was selected according to the close similarity of raw material composition. The simulation showed 51 % of oil yield at 500 °C while the experiment of Heo et al. (2010) was about 54 %. The simulation result was significantly closer to the experiment at 550 °C. It was observed that there was a correlation between the product compositions given by the simulation and the collected data from the pilot plant. As it can be seen that the correlation between the product compositions given by the simulation and the pilot plant was high. The result shows the closure of bio-oil yield between this simulation and referred experiments at 500 – 550 °C.

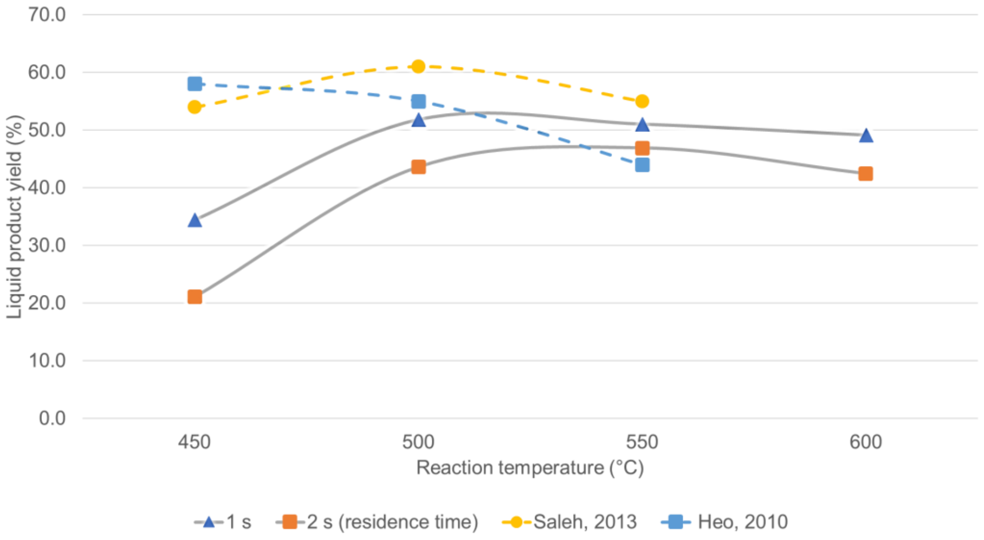

Figure 3: *Comparison of liquid product yield of fast pyrolysis between simulation and previous works*.

At 450 °C of reaction temperature, the results showed a significant difference between simulation and reported studies. The study of operating parameters can be explained that at 450 °C is the condition between slow pyrolysis and fast pyrolysis. With 1-2 s residence time in this works scope may not satisfy the optimal condition of pyrolysis and its kinetics model. The agreement between the model simulation and experimental data at fast pyrolysis condition was satisfactory but more simulation data such as difference composition of raw material and effect of other minor parameters are still required to confirm this model in order to make it more comprehensive and reliable.

4. Conclusion

A kinetic model process simulation of fast pyrolysis has been developed with Aspen Plus® to simulate and analyse fast pyrolysis for sawdust as bio-oil feedstock. The data of feedstock were based on experimental data gained from the pyrolysis plant. The product yield of fast pyrolysis of lignocellulosic biomass was calculated from developed pyrolysis reactions. The result of this model showed that it was suitable for predicting fast pyrolysis reactions for lignocellulosic biomass feedstock at high temperatures (500 – 600 °C) with low residence times (1-2 s). Moreover, this model can be used for calculating pyrolysis products without the need for experimental data with less than 10 % difference in oil product yield. The kinetics will determine how fast the reaction is approaching and the residence time will determine whether the equilibrium conditions are obtained. The products of the simulation were analysed and compared with the experiment and showed reliable results with a significant trend as an experimental result at a 95 % confidence interval. This fast pyrolysis model appeared to offer rapid assessment for energy projects associated with the transition towards low-carbon development in Asia.

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