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Residual Minimization Approach for Kinetics Parameter Estimation for Hydrogen Production from Gasification of Palm Kernel Shell

Tigabwa Y. Ahmed[a], Murni M. Ahmad*[a], Hon Loong Lam[b], Suzana Yusup[a]

[a]Universiti Teknologi PETRONAS, Green Technology Mission Oriented Research, 31750 Tronoh, Malaysia.
[b]University of Nottingham, Malaysia Campus, Department of Chemical and Environmental Engineering, 43500 Semenyih, Malaysia.
murnim@petronas.com.my

Hydrogen economy has become more attractive with the energy crises and environmental issues associated with fossil fuel utilization more so with the discovery that hydrogen can be produced from renewable biomass. This provides good prospects to Malaysia that generates abundant palm wastes. Nevertheless, there is still limited knowledge on kinetics parameters for hydrogen production from palm kernel shell gasification. In this work, a residual minimization approach has been developed to estimate the kinetics parameters for steam gasification of palm kernel shell into hydrogen. For this purpose, a mathematical model has been developed to describe the kinetics of steam gasification of palm kernel shell with in-situ CO_2 capture while considering tar formation. In addition, the effect of gasification temperature, steam/biomass ratio, and sorbent/biomass ratio on the process efficiency is profiled using the calculated kinetics parameters. The parametric study indicates that the three variables promote hydrogen production at different degree of influence.

1. Introduction

Hydrogen fuel has gained increasing attention in the energy sector attributable to its advantageous properties including environmentally friendly combustion characteristics and high energy content. Biomass steam gasification is an efficient and economically viable technology to convert the energy in biomass into chemical energy in the hydrogen gas (Gil et al., 1999). Generally, kinetics modelling allows predicting the process performance in terms of product gas composition. However, one prominent challenge in kinetics modelling is rate parameters data reported in the literature are very scarce and also the reported data are for gasification of either coal or various types of biomass. Because of the difference in composition of lignocellulosic components of every biomass or coal, the use of similar reported rate parameter data for the purpose of predicting performance of gasification of a certain biomass is hazardous. Hence, to tackle such a problem, the objective of this paper is to construct an optimization approach to estimate the kinetics parameters for the steam gasification of palm kernel shell. The basis for the parameter fitting is a kinetics model developed by the same authors which incorporated the idea of the in-situ CO_2 capture, tar formation and in-situ tar reduction.

2. Kinetics parameter fitting

An optimization model is used to calculate the kinetics parameters for the gasification process via fitting the model prediction on the product gas compositions with the experimental values reported by Li et al.

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(2009) (Table 1). This model minimizes the residual between model prediction values and the experimental data by changing values of kinetics rate parameters in the model until a desired deviation tolerance is reached (Eq. (1)). The optimization is performed using a built-in numerical optimizer in MATLAB software called *fminsearch*. The developed kinetic model consisted of ordinary differential equations solved using solver in MATLAB called ODE15. Figure 1 illustrates the optimization framework applied to the kinetics parameter fitting.

$$\min \ MSE = \sum_{i=1}^{N} \left(\frac{y_{ie} - y_{ip}}{y_{ie}} \right)^2 \tag{1}$$

where *MSE* represents the mean square error, y_{exp}: experiment data and y_{mod}: model prediction.

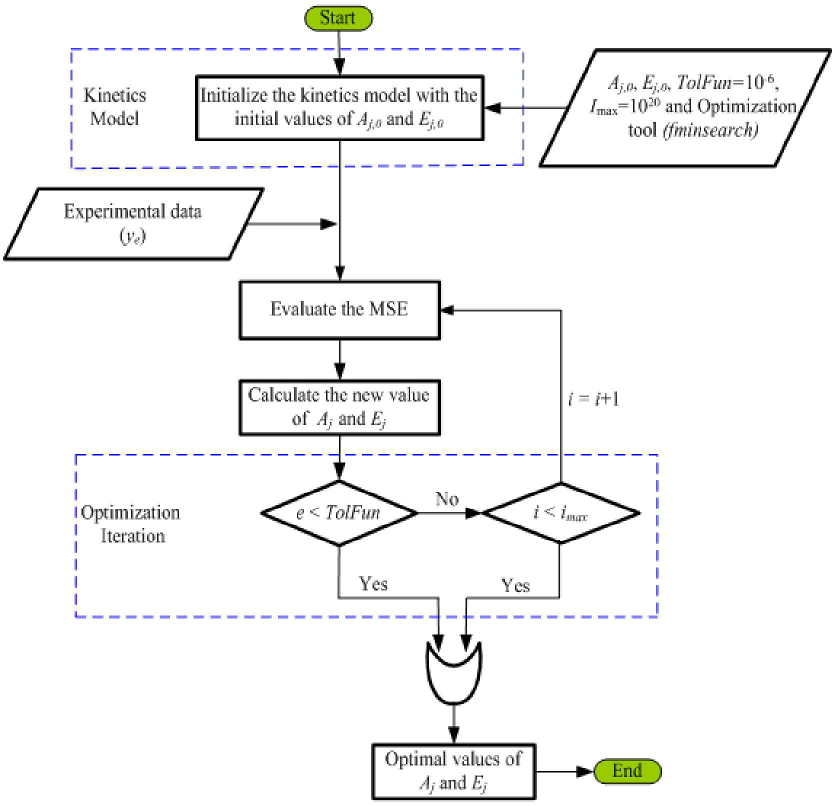

Figure 1: Optimization framework for kinetics parameter fitting

Deviation analysis of product gas composition within the selected range of temperature and steam/biomass ratio is performed using Eqs. (2) and (3) (Nikoo and Mahinpey, 2008) and hydrogen yield efficiency, Eq. (4) (Li and Suzuki, 2010), is used to evaluate the process.

$$MRSS = \frac{MSS}{N} \tag{2}$$

$$\text{Mean error} = \sqrt{MRSS} \tag{3}$$

$$H_2 \text{ yield efficiency} = \frac{H_2 \text{ yield in product gas (g)}}{\text{Biomass fed into the system(kg)}} \tag{4}$$

Table 1: Operating conditions for kinetic parameter fitting

Operating conditions	The present model	Li et al. (2009)
Biomass	Palm kernel shell	Palm oil waste
Biomass feed rate (g/hr)	300	300
Gasification agent	Steam/Catalytic	Steam/Catalytic
Temperature range (°C)	750-900	750-900
Pressure (atm)	1	1
Steam/biomass ratio (g/g)	1.33	1.33

3. An overview of the developed kinetics model

A kinetics model for steam gasification of palm kernel shell is developed on the basis that there exist two zones in the gasifier i.e. pyrolysis zone (200-450°C) and gasification zone (450-900°C) Ahmed et al. (2012). The sum of the tars released during pyrolysis is represented by a surrogate model compound, toluene (C_7H_8) (Swierczyski et al., 2007). Calcium oxide is the adsorbent used for the in-situ CO_2 capture. The developed kinetics model equations are solved using ordinary differential equation solver in MATLAB, ODE15s. Table 2 lists the chemical reactions considered in the model. The kinetics model equation for a component i involved in reactions both in the pyrolysis and gasification zone is formulated as in Eq. (5) (Kaushal et al., 2010):

$$\frac{dNi}{dt} = VR_i \tag{5}$$

where N_i is the number of moles of component i , V is the reactor volume which is considered constant and R_i is the molar rate of production of component i per unit volume and is defined as follows (Corella and Sanz, 2005):

Table 2: Chemical reactions considered in the model

Process	Chemical reaction	*ΔH* *ΔH_r (heat of reaction, kJ/mol)*	Ref.
Pyrolysis	$PKS \xrightarrow{k_1} Gas$ $PKS \xrightarrow{k_2} Tar$ $PKS \xrightarrow{k_3} Char$	> 0 > 0 > 0	Thurner and Mann (1981)
Gasification	$C + CO_2 \xrightarrow{k_4} 2CO$	+172 (at 298 K)	Choi et al. (2001)
	$C + 2H_2 \xrightarrow{k_5} CH_4$	-75 (at 298 K)	Choi et al. (2001)
	$C + H_2O \xrightarrow{k_6} CO + H_2$	+131.5 (at 298 K)	Corella and Sanz (2005)
	$CH_4 + H_2O \xrightarrow{k_7} CO + 3H_2$	+206 (at 298 K)	Corella and Sanz (2005)
	$CO + H_2O \xleftrightarrow{k_8 \,\&K_w} CO_2 + H_2$	-41 (at 298 K)	Corella and Sanz (2005)
In-situ CO_2 capture	$CaO + CO_2 \xrightarrow{k_9} CaCO_3$	-178.3 (at 298 K)	Ar and Dogu (2001)
Steam tar reforming	$C_7H_8 + 7H_2O \xrightarrow{k_{10}} 7CO + 11H_2$	+876 (at 1173K)	Swierczyski et al. (2007)
Tar cracking	$Tar\,(C_7H_8) \xrightarrow{k_{11}} CH_4$	> 0	Kaushal et al. (2010)

4. Results and discussion

Table 3 presents the value of the kinetics rate parameters, A_j and E_j, obtained via residual minimization. These values are next used in the parametric study performed to evaluate the process performance with respect to process variables including gasification temperature, steam/biomass ratio and sorbent/biomass ratio.

Table 3: The value of the kinetic rate parameters calculated using the residual minimization approach

k_j	*A_j [s^{-1}]*	*E_j [kJ/mol]*	*min MSE*
k_1	1.4931E+4	82.8049	
k_2	3.9759E+6	125.7897	
k_3	7.6103E+5	102.1827	
k_4	5.1333	1.3333E+6	
k_5	0.1182	150.2318	
k_6	2.0266E+5	40.7142	**0.0848**
k_7	287.2077	142.6859	
k_8	1.0507E+6	54.7729	
k_9	10.2940	0.3837	
k_{10}	8.3173E+9	56.4357	
k_{11}	8.5549E+3	76.4857	
$Kw = 8.7825\exp(-57.7466/T)$			

4.1 Effect of temperature

Figure 2 shows gasification model simulation results using the calculated kinetics parameters together with the experimental results by Li et al. (2009). The model prediction agrees well with experimental data and the mean error for each component based on the fitting on the temperature parametric study is given in Table 4. The increase in temperature enhances hydrogen content in the product gas. The endothermic steam methane reforming, steam tar reforming, gasification reactions of the char and water-gas reactions which are favorable at high temperatures led to the increase in hydrogen production. According to the Le Chatelier's principle for endothermic reactions, an increase in temperature facilitates product formation resulting in an increase in H_2 content and a decrease of CH_4 content in the product gas. At high temperatures the product gas composition is dominated by the water-gas shift reaction. The produced CO is consumed in this reaction leading to decrease in its content in the product gas and slight increase in CO_2 composition.

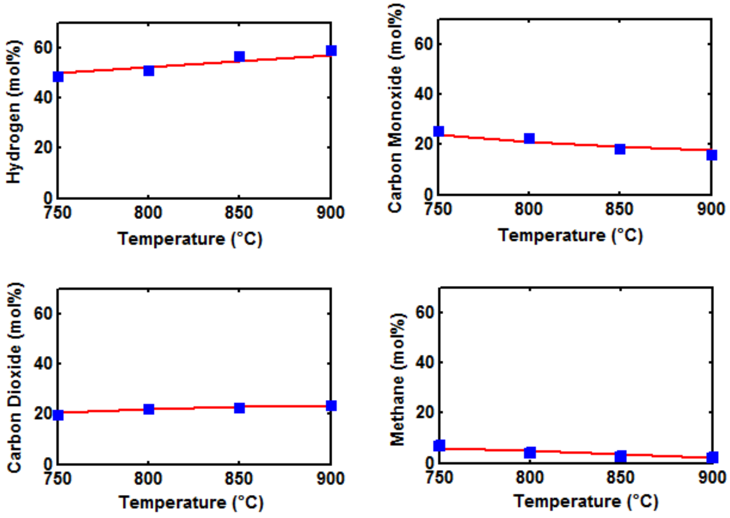

Figure 2: Effect of temperature on product gas composition (— Model, ■ Li et al. (2009))

Table 4: Mean error for each component based on the fitting on the temperature parametric study

Operating variable	Mean Error			
	H_2	CO	CO_2	CH_4
Gas composition versus temperature	0.030	0.092	0.034	0.165
Gas composition versus steam/biomass ratio	0.059	0.202	0.084	0.532

4.2 Effect of Steam/biomass ratio

Figure 3 illustrates the effect of the steam/biomass ratio on product gas composition at a gasification temperature of 900°C. The increase in the steam/biomass ratio enhances hydrogen production attributed to the utilization of the hydrogen content of steam in the reforming and shift reactions. The addition of steam favors tar and char reduction and the increase of the gas yields mainly results from tar steam reforming, cracking and char gasification. On the other hand, the amount of CO and CH_4 decrease which could be explained by more steam reforming reactions of CO and CH_4 taking place because of the increased in steam quantity. Moreover, the presence of a large excess of steam drives the water-gas shift reaction to the right leading to an increase in H_2 and CO_2 and decrease in CO concentration with the rise of temperature.

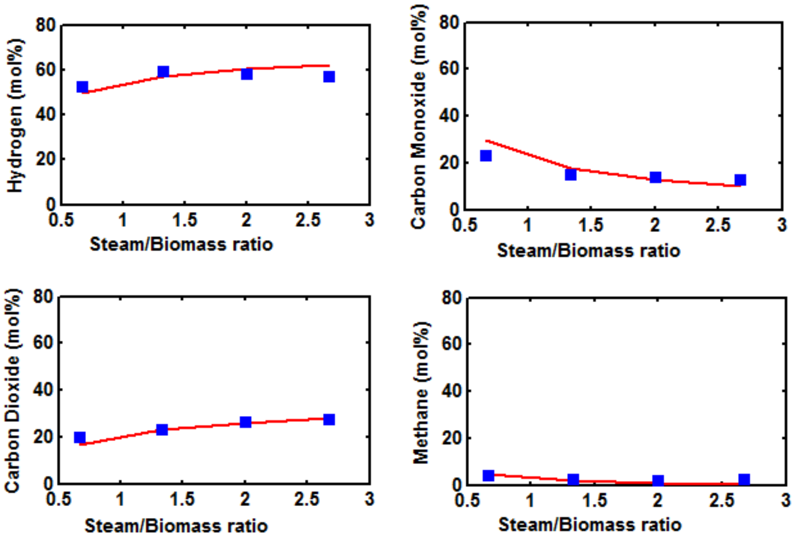

Figure 3: Effect of steam/biomass ratio on product gas composition (— Model, ■ Li et al. (2009))

4.3 Effect of sorbent/biomass ratio on hydrogen yield efficiency

Figure 4 shows the hydrogen yield efficiency as a function of both temperature (750°C to 900°C) and steam/biomass ratio (0.5 to 3) with CaO/biomass ratio of 1. At temperature of 900°C, steam/biomass ratio of 3 without CaO, hydrogen yield of 125.3 g/kg and with CaO/biomass of 1 yield of 133 g/kg of PKS can be produced. The CO_2 capture brings significant increase on the hydrogen yield. Comparison with literature is presented in Table 5 and the yield is comparable to the reported data. The deviation is due to the CO_2 capture included in the present study which alters the product gas composition consequently promoting hydrogen production.

Table 5: Comparison of hydrogen yield with literature data

Biomass	Gasification	H_2 (g/kg of biomass)	Approach	Ref
Palm oil waste	Steam + catalyst	116.14	Experimental	Li et al. (2009)
PKS	Steam + catalyst + CaO	133.1	Present model	

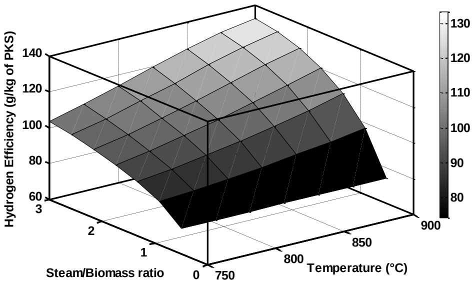

Figure 4: Surface plot for effect of temperature and steam/biomass ratio on hydrogen yield efficiency

5. Conclusion

The developed residual minimization approach is effective to calculate the kinetic parameters for steam gasification of palm kernel shell with in-situ CO_2 capture and tar reduction. The kinetics parameters were next used to investigate the effect of the gasification temperature and steam/biomass ratio on the process performance in terms of hydrogen yield efficiency. Results from this study showed that the increase in temperature, steam/biomass ratio and sorbent/biomass ratio enhanced hydrogen content and yield in the product gas.

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