Int. J. Environ. Res., 7(1):97-104, Winter 2013
ISSN: 1735-6865

Gasification Kinetics of Date palm seed using Carbon Dioxide

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Received 17 Jan 2012; Revised 2 Aug. 2012; Accepted 14 Aug. 2010

ABSTRACT: Gasification is a well-known reaction owing to its relevance to generation of sustainable energy from biomass and development of porous carbons. The present paper attempts to experimentally investigate the kinetics of palm shell char gasification using carbon dioxide (CO_2) in a controlled environment using Thermo Gravimetric Analyzer (TGA) at temperatures ranging from 800 to1000°C. A relevant kinetic model representing the experimental data was identified by fitting the experimental data with popular semi empirical kinetic models such as Linear Model (LM), Volume Reaction Model (VRM), Shrinking Core Model (SCM), and Random Pore Model (RPM). The model kinetic parameters were evaluated by minimizing the sum of root mean square error (RMSE). Among the models tested the RPM exhibited very close adherence to the experimental data evidenced from the minimum RMSE of 0.0046. The ability of the RPM model to represent the gasification kinetics was attributed to its ability to account for the pore growth during initial stages of gasification and destruction of pores due to coalescence in later stages of gasification. The rate of reaction increased with increase in temperature and activation energy was found to be 64.5 KJ/mol.

Key words: Gasification, Date Palm Seed char, Pyrolysis, Activation energy, Kinetic models

INTRODUCTION

The date palm seeds are one of the major agro-based residues produced in huge quantities in the Gulf region. The gasification is a process of converting solid fuel into gaseous product mainly involving two sequential operations which are (i) conversion of cellulosic compounds into a carbon rich product by eliminating the volatile components in an inert environment generally known as pyrolysis followed by (ii) the reaction of the carbon rich product with steam, CO_2 or air. The gasification reactions with steam produce synthesis gas (mix of H_2 and CO) while the reaction with CO_2 result in conversion to carbon mono oxide, which are base molecules for the Fisher Tropsch synthesis, utilized for conversion of syngas in to liquid fuels.

In general the literature on gasification kinetics addresses effect of parameters such as gasification temperature, particle size, char porosity, mineral content of the char, temperature and partial pressure of the gasifying agents (Wu, Bryant *et al.,* 2000; Ollero, Serrera *et al.,* 2002; Mermoud, Salvador *et al.,* 2006). A number of studies have reported the ability of the gasification process to produce high surface area activated carbon either in presence of CO_2 or steam or combination of both at high temperatures (Garcia, Salvador *et al.,* 2001; Ahmed and Gupta 2010). The literature relevant to palm shell utilization is limited to conversion in to activated carbon (Juang, Wu *et al.,* 2000; Girgis and El-Hendawy 2002; Haimour and Emeish 2006; El Nemr, Khaled *et al.,* 2008; Zhang, Hara *et al.,* 2010). To the knowledge of authors the kinetics of palm char gasification has not been reported in open literature, a proper estimation of the kinetics parameters is essential for the design, scale up and for optimization of process parameters (Cetin, Gupta *et al.,* 2005; Zhang, Hara *et al.,* 2010). In general estimation of reaction kinetics involves experimental measurements of either the gas phase concentration or the solid phase weight loss with respect to time. Most popularly adopted method for kinetic studies, involve utilization of TGA as it can precisely control the reaction conditions as well as monitor the weight loss with respect to time with impeccable accuracy. The char reactivity depends on three main characteristics of the sample: chemical structure, inorganic constituents and porosity. In general the well-known kinetic models do not include basic reaction mechanism, as the intermediate components are difficult to measure and are variable with the conversion level. Hence the

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practical approach being utilization of global reaction kinetics which accounts only the interaction between solid and gas phase. Some of the recent work on CO_2 gasification kinetics has been reported that the gasification kinetics of pine and birch chars (Khalil, Vaìrhegyi *et al.,* 2008) under controlled conditions using TGA, while coal char gasification (Dutta, Wen *et al.,* 1977) reported using simple homogeneous kinetic model with the order of reaction being one for both the reactants (Carbon and CO_2) and lignite char gasification (Shufen and Ruizheng 1994) with CO_2, H_2 and H_2O mixtures under pressure. They have highlighted the suitability of shrinking core model for steam and carbon dioxide reaction, while VRM for the reaction with hydrogen. The kinetic parameters sourced from literature on CO_2 gasification reaction, show a wide span of apparent activation energies for biomass char ranging from 18.7 KJ/mol (Mani, Mahinpey *et al.,* 2011) to 318 KJ/mol (Blackwood and Ingeme 1960). The aim of this work is to experimentally investigate the kinetics of date palm seed char-CO_2 reaction under controlled conditions using TGA and to propose an appropriate kinetic model that could well represent the experimental data. To the knowledge of the authors no such kinetic study pertaining to date palm seed char CO_2 gasification has been reported in the open literature.

MATERIALS & METHODS

Date palm seed char was prepared by heating crushed date palm seeds in a tubular furnace at 800p C under the nitrogen flow. The samples were loaded in furnace and heated at the rate of 20°C/min until it reached the desired temperature of 800p C under the nitrogen flow. The samples were left for one hour upon reaching 800p C and were cooled to the room temperature with the continued flow of nitrogen. The yield of carbon was consistently found to be around 19% ensuring stability of the experimental conditions. The carbon samples were ground to a uniform size, sieved to a size range of 300-500mm and stored for gasification experiments. The composition of date palm seed char is shown in Table 1. The gasification experiments were conducted using TGA, The date palm seed char of about 15 mg was taken in a small glass crucible and placed in the middle of the reaction zone. The char sample was initially heated in nitrogen atmosphere at a heating rate of 30p C/min until the desired reaction temperature was achieved. Upon reaching the desired temperature the CO_2 gas was introduced by shutting the N_2 flow, at the rate of 20cc/min. The char-CO_2 reaction was continued for one hour by maintaining constant reaction temperature. Experiments were conducted at reaction temperature of 800p C, 900p C, and 1000p C. The weight loss with respect to time was acquired using the Thermal Acquisition software Version 1.3.2.2, which was utilized to establish the reaction kinetics.

Table 1. Composition of date palm seed char (Girgis and El-Hendawy 2002)

Compound	%
Carbon	84.5
Hydrogen	2.2
Nitrogen	4.1
Oxygen	3.6
Ash content	5.6

The char gasification reaction can be represented as,

$$C + CO_2 \longrightarrow 2CO$$

The choice of a good kinetic model is based on its ability to closely match the experimental data with limited mathematical complexities. Hence in order identify the appropriate kinetic model that could explain the reaction kinetics of date palm shell char with CO_2, different popular/simple kinetic models such as Linear model (LM), Shrinking Core Model (SCM), Random Pore model (RPM), and Volume Reaction Model (VRM) were tested with the experimental data.

The carbon conversion (X) and the reactivity were calculated by using eqs. (1),

$$dX / dt = k(T) f(X) \quad (1)$$

where dX/dt is the rate of reaction, k is the rate constant based on the gas temperature, while f(X) accounts for the partial pressure of gasifying agent (CO_2) and the changes in the physical or chemical properties of the sample as the gasification proceeds. If the concentration of gasifying agent is held constant during the process, the f(X) term accounts only for the changes in the physical or chemical properties of the sample, which have been accounted by various models. In the present work four models were tested with the experimental data and their appropriate variations in the f(X) terms have been detailed below.

The Volume Reaction Model (VRM) (Seo, Lee *et al.,* 2010) assumes a homogenous reaction throughout the char particle. This model is simple and assumes uniform gas diffusion in the entire particle, and simplifies the heterogeneous gas-solid reaction of carbonaceous material with carbon dioxide. The kinetic expression for reaction rate is described as follows:

$$X = 1 - \exp(-k_v t) \quad (2)$$

The Shrinking Core Model (SCM) (Seo, Lee *et al.,* 2010) assumes the particles to be spherical and that the reaction occurs initially on the external surface of char and gradually moves into the inner surface. The kinetic expression for reaction rate is described as follows:

$$X = 1 - (1 - \frac{k_s t}{3})^3 \qquad (3)$$

The Random Pore Model (RPM) (Fermoso, Stevanov *et al.,* 2009) **c**onsiders the overlapping of pore surfaces, which results in reduction in the area (Garcia, Salvador *et al.,* 2001) available for reaction. This model can predict maximum reactivity as the reaction proceeds and accounts for pore growth during the initial stages of gasification and destruction due to coalescence of adjacent pores during the later stages. The reaction rate can be described as follows:

$$X = 1 - \exp\left[- k_r t(1 + \frac{k_r \psi t}{4}) \right] \qquad (4)$$

The model parameters are kinetic constant k_r, and pore structure related parameter ψ, which depends on the pore length, surface area and porosity of carbon.
The linear model (LM) shown as below,

$$X = kt \qquad (5)$$

Considers the gasification reaction to only depend on the gasification temperature, with the linear dependence of conversion with time. The suitability of the models detailed above, for the gasification reaction was tested by fitting the experimental data (% conversion vs time) with the model prediction. The kinetic parameters were estimated by minimizing the RMSE of model prediction with the experimental data. The RMSE is defined as,

$$RMSE = \sqrt{(X_{\exp} - X_{pred})^2 / (N-1)} \qquad (6)$$

The X_{exp} and X_{pred} are the experimental and model predicted %. The suitability of the model is assessed based on the minimum of error between the experimental data and the model prediction evidenced from the lowest of the RMSE.

RESULTS & DISCUSSION

The rate of char gasification reaction was expressed in such a way that the rate depends on the char conversion. The CO_2 gas flow rate was maintained constant throughout the reaction. The kinetic of char gasification using TGA was conducted to derive the intrinsic reactivity at a relatively low temperature in the chemically controlled reaction regime. The experimental data from TGA, is shown as reaction time vs. percentage char conversion in Fig. 1. The figure shows an increase in % conversion with increase in the reaction time and reaction temperature, in line with the basic understanding of reaction kinetics. In order to identify an appropriate kinetic model that can suitably represent the experimental data, various models like VRM, SCM, LM and RPM were tested. Among the models tested RPM model was found to match the experimental data satisfactorily with the lowest of RMSE in the range of 0.0046 to 0.0118 for all the three sets of data. 'ψ' was the parameter related to porosity and surface area of the char and it was estimated by fitting the model equation with the experimental data, by minimizing the RMSE value as stated in eq. (6). The consistency of the increase in fit value of ψ with increase in the temperature was validated with the increase in the surface area and porosity of the carbon with increase in the temperature. The ψ was defined as $\psi = 4\pi L (1-\varepsilon)/S^2$, where 'ε' is the porosity, 'S' is the surface area and 'L' average micropore diameter (diameter or length) of the carbon. It can be observed from the relation that Ψ is proportional to (1-ε) and inversely proportional to S^2. The fit of model with experimental data predict the Ψ to decrease from 19.58 (800p C) to 6.77 (1000p C) which confirms the increase in porosity and surface area of the char formed at high temperatures. The kinetic constants estimated at different temperatures were utilized to estimate the activation energies of date palm seed char gasification with CO_2. The activation energy and pre-exponential factors are tabulated in Table 2.

Table 2. Kinetics data for various models

S.NO	Model	$K_{800\,^{\circ}C}$	$K_{900\,^{\circ}C}$	$K_{1000\,^{\circ}C}$	E	A	RMSE
1	RPM	0.003300 Ψ(19.58)	0.005859 Ψ(7.50)	0.010300 Ψ(6.77)	64.5	4.49	0.00466-0.01188
2	SCM	0.005317	0.008018	0.015422	59.9	4.18	0.01507-0.03088
3	VRM	0.005513	0.008474	0.017106	63.7	6.58	0.01727-0.04234
4	LM	0.004941	0.007161	0.012410	51.9	1.59	0.00978-0.01264

E: Activation Energy, KJ/mol; A: Pre-exponential factor, min^{-1}; K: kinetic constant, min^{-1}

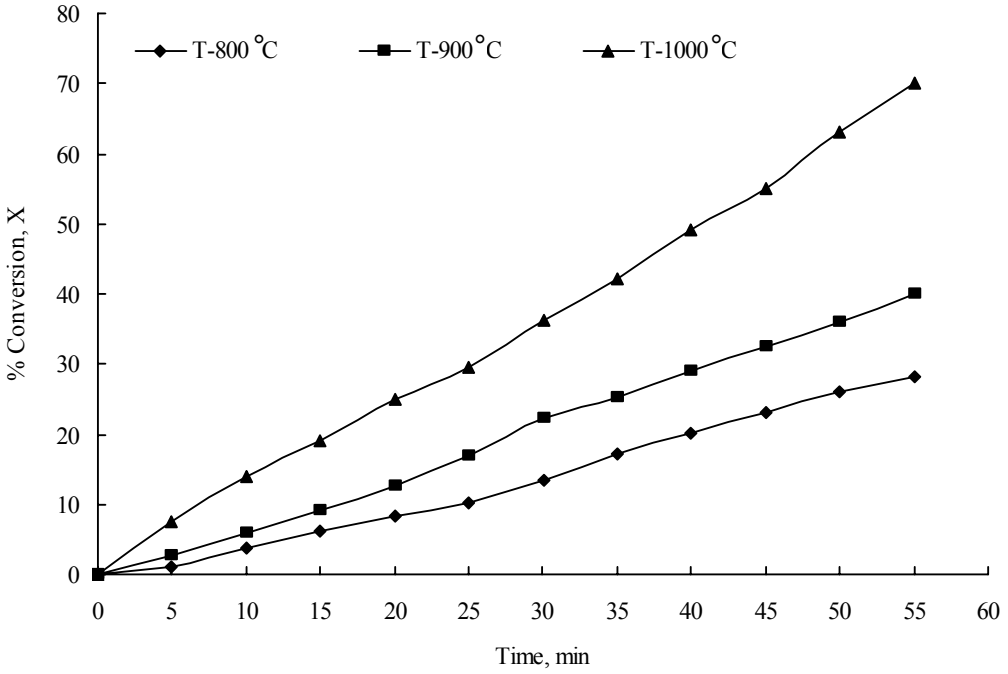

Fig. 1. Effect of gasification temperature on the % conversion of date palm seed char

The temperature range covered in the present study (800p C-1000p C), are generally considered to be low gasification temperatures, where the rate of diffusion of CO_2 doesn't offer significant mass transfer resistance to the overall kinetics of the reaction, and are termed as chemically controlled regime (Liu, Fang *et al.,* 2008). As reported in the literature (Haykiri-Acma and Yaman 2007) Fig. 2 shows the decrease in Ψ with increase in the temperature of the gasification reaction. The increase in gasification temperature would increase the rate of C-CO_2 reaction, resulting in higher % conversion. It was well known that higher conversion of char-CO_2 reaction will increase the porosity of the carbon, which intern will result in higher surface area of the carbon. Char-CO_2 reactions are popularly utilized in industries to commercially manufacture microporous carbon, with high surface area. Ψ has decreasing dependency with increase in the porosity and the surface area of the carbon. BET surface area of the resultant char at the end of the reaction time was estimated by generating nitrogen adsorption isotherm, using Quantachrome surface area analyzer, adopting standard adsorption procedures (Suresh Kumar Reddy, Sreedhar et al. 2008). Fig. 2 shows a sharp decrease in ψ with the increase in temperature from 800 to 900°C, while there is only a marginal decrease with further increase from 900 to 1000°C. The BET surface area of char was estimated to be 260 m^2/g at 800p C, while at 1000p C as 980 m^2/g respectively. The low porosity with low surface area contributes to the high value of ψ, while the low value of ψ at higher temperature can be attributed to the high porosity and surface area. Although the experimental data were found to match with the RPM model as compared to other models, the estimation of activation energy was estimated based on all the four models, as it involves only capturing the effect of temperature on the reaction kinetics. The activation energy was found to approximate to 64.5 KJ/mol. The comparisons of the model prediction with the experimental data for all the three models are shown in the Fig 3 to 6. It can be seen from figures that the RPM model matches well with the experimental data at all temperatures, while the other models are better at lower temperature, but fall short at higher temperatures. Although the LM was able to fit the experimental data as close to the RPM model, the fundamental concepts of the LM is weak as it doesn't account the physical and chemical changes of the char during gasification.

Table 2 summarizes the model parameters along with the RMSE errors for all the four models. The ability of RPM model to match closely with the experimental data could be attributed to the ability of the model to account for the pore growth during the initial stages of gasification and destruction of pores due to coalescence of adjacent pores in later stages of gasification. From the Arrhenius plot shown in Fig. 7

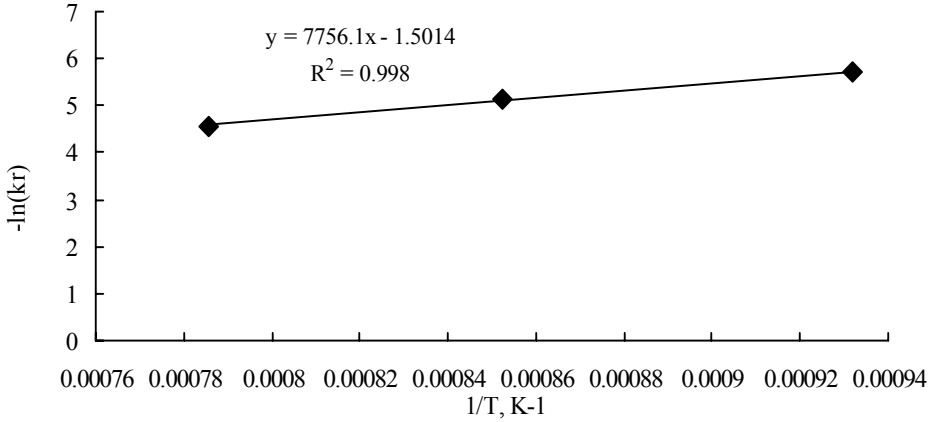

Fig. 2. Variation of RPM model parameter Psi (ψ) with gasification temperature

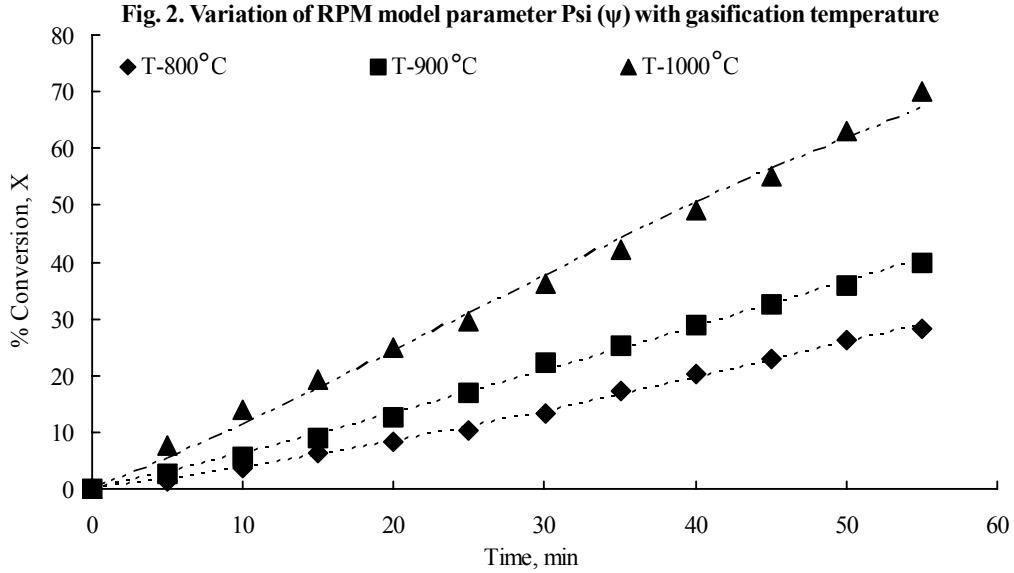

Fig. 3. Comparison of experimental data with the model prediction due to RPM at different gasification temperatures (Lines: Model Prediction conversion)

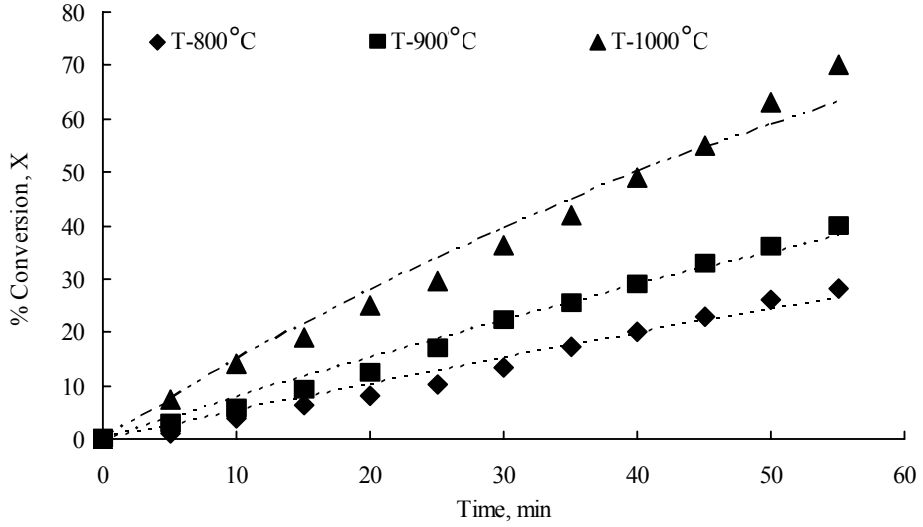

Fig. 4. Comparison of experimental data with the model prediction due to SCM at different gasification temperatures (Lines: Model prediction conversion)

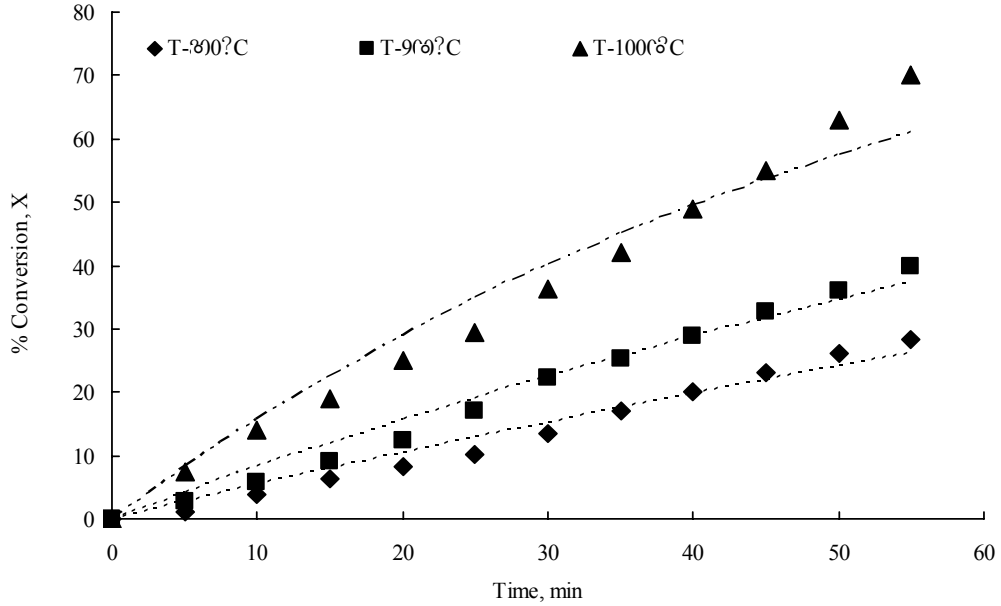

Fig. 5. Comparison of experimental data with the model prediction due to VRM at different gasification temperatures (Lines: Model prediction conversion)

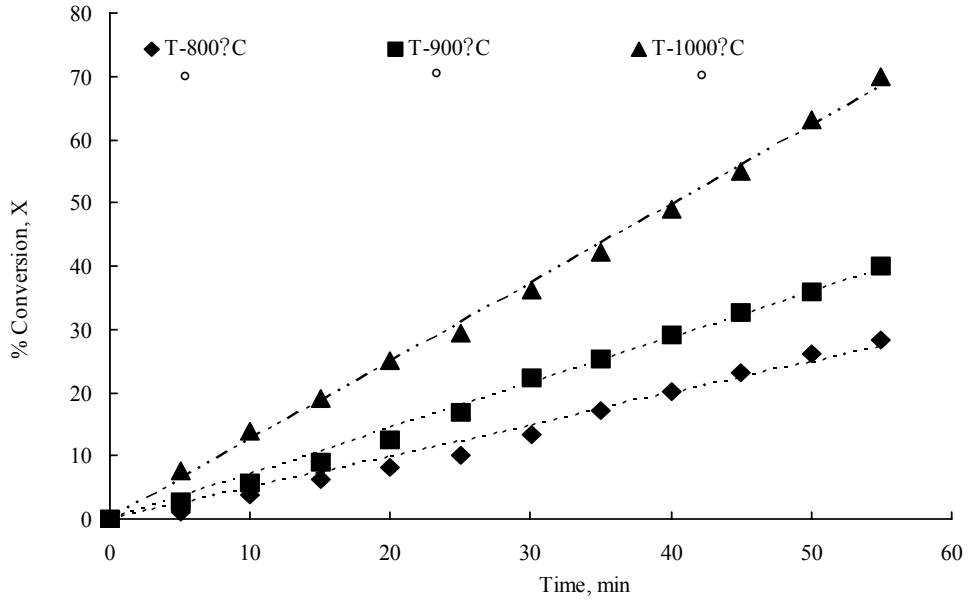

Fig. 6. Comparison of experimental data with the model prediction due to LM at different gasification temperatures (Lines: Model prediction) conversion

the activation energy for the date palm seed char-CO_2 gasification reaction was estimated to be 64.5 KJ/mol. Table 3 compiles the literature reported activation energies for various biomass based gasification reactions and it is found to vary in a wide range from 18.7 to 184.0 KJ/mol. The activation energies of the biomass char were found to vary based on source of biomass and possibly could be attributed to the large variation in the inorganic content of the biomass. Generally the low activation energies indicate high reactivity of the char which could only be attributed to the inherent variation in the composition of the

Table 3. Comparison of Activation energies of Date Palm seed char with the other biomass reported in literature

S.NO	Material	Activation Energy, KJ/mol	Reference
1	Date palm seed char	64.5	Present study
2	Wheat straw	18.7	(Mani, Mahinpey et al. 2011)
3	Pinus densiflora	134.0	(Seo, Lee et al. 2010)
4	Pinus elliottii	184.0	(Fermoso, Stevanov et al. 2009)
5	Thai-lignite char	136.5	(Liu, Fang et al. 2008)
6	Rice Husk power	83.0	(Bhat, Ram Bheemarasetti et al. 2001)
7	Japanese wood	94.0	(Matsumoto, Takeno et al. 2009)
8	Corn cob char	160.0	(Gaur, Rao et al. 1992)

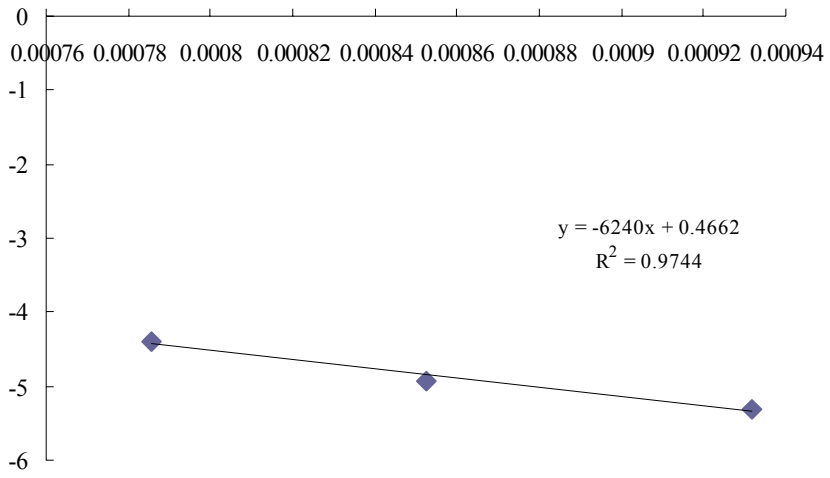

Fig. 7. Arrhenius plot using kinetic parameter estimated using Random Pore Model (RPM)

biomass. The variation in activation energies was attributed to the variation in inorganic content (Mani, Mahinpey *et al.*, 2011).

CONCLUSION

The date palm char gasification reactions with CO_2 was performed using conventional TGA covering a temperature range of 800 to 1000°C at a constant flow rate of CO_2. The extent of C-CO_2 reaction was found to increase with increase in the gasification temperature. The rate of reaction was modeled using various popular kinetic models such as the LM, VRM, SCM and RPM. Among all the models RPM was found to match the experimental data with the minimum of error as compared to other models. The RMSE for the RPM was found to be in the range of 0.0046 to 0.0118 while for the other models were found be higher. The ability of the RPM model to represent the gasification kinetics was attributed to its ability to account for the pore growth during initial stages of gasification and destruction of pores due to coalescence in later stages of gasification. The activation energy was estimated to be 64.5 KJ/mol. The activation energy for date palm biomass char was found to be moderate as compared with other biomass.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support received from The Petroleum Institute and for

giving an opportunity to work on Activated carbon research.

REFERENCES

Ahmed, I. I. and Gupta, A. K. (2010). Pyrolysis and gasification of food waste: Syngas characteristics and char gasification kinetics. Applied Energy, **87 (1)**, 101-108.

Blackwood, J. and Ingeme, A. (1960). The Reaction of Carbon with Carbon Dioxide at High Pressure. Australian Journal of Chemistry, **13 (2)**, 194-209.

Cetin, E., Gupta, R. and Moghtaderi, B. (2005). Effect of pyrolysis pressure and heating rate on radiata pine char structure and apparent gasification reactivity. Fuel, **84 (10)**, 1328-1334.

Dutta, S., Wen, C. Y. and Belt, R. J. (1977). Reactivity of Coal and Char In Carbon Dioxide Atmosphere. Industrial & Engineering Chemistry Process Design and Development, **16 (1)**, 20-30.

El Nemr, A., Khaled, A., Abdelwahab, O. and El-Sikaily, A. (2008). Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. J Hazard Mater, **152 (1)**, 263-275.

Fermoso, J., Stevanov, C., Moghtaderi, B., Arias, B., Pevida, C., Plaza, M. G., Rubiera, F. and Pis, J. J. (2009). High-pressure gasification reactivity of biomass chars produced at different temperatures. Journal of Analytical and Applied Pyrolysis**, 85 (1–2)**, 287-293.

Garcia, L., Salvador, M. L., Arauzo, J. and Bilbao, R. (2001). CO_2 as a gasifying agent for gas production from pine sawdust at low temperatures using a Ni/Al coprecipitated catalyst. Fuel Processing Technology, **69 (2)**, 157-174.

Girgis, B. S. and El-Hendawy, A. N. A. (2002). Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid. Microporous and Mesoporous Materials, **52(2)**, 105-117.

Haimour, N. M. and Emeish, S. (2006). Utilization of date stones for production of activated carbon using phosphoric acid. Waste Management, **26 (6)**, 651-660.

Haykiri-Acma, H. and S. Yaman (2007). Interpretation of biomass gasification yields regarding temperature intervals under nitrogen–steam atmosphere. Fuel Processing Technology, **88(4),** 417-425.

Juang, R. S., Wu, F. C. and Tseng, R. L. (2000). Mechanism of Adsorption of Dyes and Phenols from Water Using Activated Carbons Prepared from Plum Kernels. Journal of Colloid and Interface Science, **227 (2)**, 437-444.

Khalil, R., Vairhegyi, G. B., Jaschke, S., Grønli, M. G. and Hustad, J. (2008). CO_2 Gasification of Biomass Chars: A Kinetic Study. Energy & Fuels, **23 (1)**, 94-100.

Liu, T. F., Fang, Y. T. and Wang, Y. (2008). An experimental investigation into the gasification reactivity of chars prepared at high temperatures. Fuel, **87 (4–5)**, 460-466.

Mani, T., Mahinpey, N. and Murugan, P. (2011). Reaction kinetics and mass transfer studies of biomass char gasification with CO_2. Chemical Engineering Science, **66 (1)**, 36-41.

Mermoud, F., Salvador, S., Van de Steene, L. and Golfier, F. (2006). Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles. Fuel, **85 (10–11)**, 1473-1482.

Ollero, P., Serrera, A., Arjona, R. and Alcantarilla, S. (2002). Diffusional effects in TGA gasification experiments for kinetic determination. Fuel, **81 (15)**, 1989-2000.

Seo, D. K., Lee, S. K., Kang, M. W., Hwang, J. and Yu, T.U. (2010). Gasification reactivity of biomass chars with CO_2. Biomass and Bioenergy, **34 (12)**, 1946-1953.

Shufen, L. and Ruizheng, S. (1994). Kinetic studies of a lignite char pressurized gasification with CO2, H2 and steam. Fuel, **73 (3)**, 413-416.

Suresh Kumar Reddy, K., Sreedhar, I. and Raghavan, K. V. (2008). Behavior of a Deactivating HZSM-5 with Varying Al^{+3} Content in Vapor Phase Aminocyclization. Catalysis Letters, **125 (1)**, 110-115.

Wu, H., Bryant, G., Benfell, K. and Wall, T. (2000). An Experimental Study on the Effect of System Pressure on Char Structure of an Australian Bituminous Coal. Energy & Fuels, **14 (2)**, 282-290.

Zhang, Y., Hara, S., Kajitani, S. and Ashizawa, M. (2010). Modeling of catalytic gasification kinetics of coal char and carbon. Fuel, **89 (1)**, 152-157.