Kinetic model of low temperature coal tar hydrocracking in supercritical gasoline for reducing coke production

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Abstract−To reduce coke production during low temperature coal tar hydrocracking in supercritical gasoline, a lump kinetic model was derived on the basis of catalytic cracking reaction mechanism. Lumps were defined by different reaction properties. Reaction rate constants, indexes of hydrogen to coal tar ratio, indexes of gasoline to coal tar ratio, activation energies, and pre-exponential factors were estimated according to the previous experimental data. The results show that the proposed model could not only predict the product yields successfully, but also provide more information which was useful for any attempts to reduce the coke content and promote the conversion of coal tar to light oils.

Keywords: Low Temperature Coal Tar, Supercritical Gasoline, Hydrocracking, Kinetic Model, Coke

INTRODUCTION

China is a big country in coke production, with coke output in 2011 amounting to 4.28 billion tons, accounting for above 60% of the world's total output. Coal tar is an important by-product in coke production, and the coal tar output in China was 17.5 million tons in 2011. At present, coal tar is mostly used as a crude fuel, except for the small amount used to produce chemical products, which leads to serious environmental pollution due to its heteroatom contents such as sulfide and nitride. Therefore, it is of vital importance to convert coal tar to high-clean fuel oils such as gasoline and diesel.

The processes for converting coal tar to light oil have been investigated by many researchers [1-7]. Supercritical fluids have been attractive for application in the coal tar conversion process due to their favorable characteristics. Han et al. [8] and Ma et al. [9] studied that supercritical water as a solvent was introduced to low temperature coal tar hydrocracking process; the results show that supercritical water can promote the reaction rate and reaction extent due to its high mass-transfer rate and good dissolubility. According to the principle of similarity and compatibility, coal tar should have high solubility in supercritical xylene (critical temperature 357 °C and critical pressure 3.7 MPa) and gasoline (critical temperature 316 °C and critical pressure 3.47 MPa [10]) due to its high content of aromatics. More favorably, when gasoline is used as a solvent, separation of the gasoline solvent from the liquid product is not needed in coal

tar conversion. So xylene and gasoline were used as supercritical solvents in the low temperature and high temperature coal tar hydrocracking process in our previous study [11]. The results show that supercritical xylene and gasoline could improve light oil yields and inhibit coke production. However the reaction kinetic of coal tar hydrocracking in supercritical solvent has been rarely reported.

To investigate the effects of operating parameters on reaction rate and related mechanism to reduce coke during coal tar hydrocracking process in supercritical gasoline, the reaction kinetics was investigated on the basis of previous experiments, and the kinetic parameters were estimated according to the experiment data.

EXPERIMENTAL

1. Materials and Methods

Coal tar used in the experiment was obtained from the North of Shaanxi Province, China. Its properties are shown in Table 1.

The Co-Mo-Pd-Y zeolite catalyst was prepared by identical volume method [12], which contained Mo and Co of 16.33%, Co/(Co+ Mo) of 0.5, and Pd of 0.1%.

2. Reactor and Operation Procedure

The low-temperature coal tar hydrocracking reactions were carried out in a batch reactor without stirring, as shown in Fig. 1. The reactor was made of cylinder and cover that was sealed by a copper circle. The reactor cylinder was made of stainless steel with a vol-

Table 1. Properties of low temperature coal tar

Density (20 °C)/g·mL⁻¹	Viscosity (100 °C)/mm²·s⁻¹	Distillation range/°C					Moisture/%	Asphaltene/%
		IBP	10%	50%	90%	EBP		
0.9427	56.4	205	250	368	486	531	2.23	17.96

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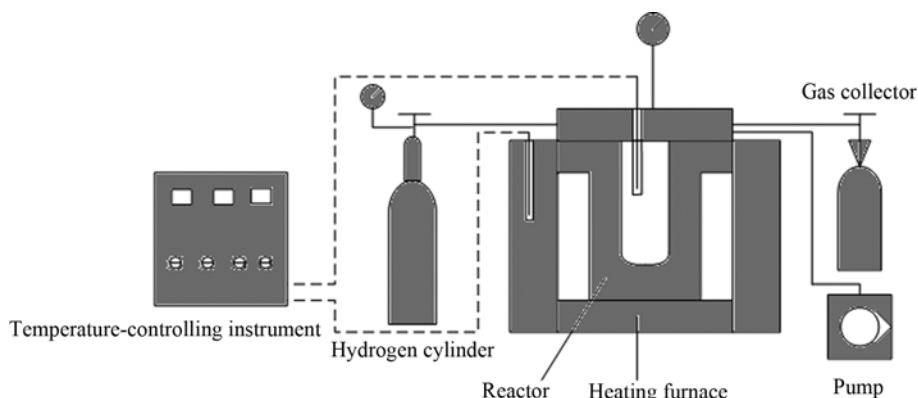E-mail: doudoueva@sina.cn

Fig. 1. Reaction apparatus diagram.

ume of 2 L, and its internal diameter and height was 10 cm and 25.5 cm, respectively. The reactor was heated by an electric stove, and its heating rate was 2.8 °C/min. The temperature of reactor was measured by a thermocouple inserted into the reactor, and the value of temperature was displayed in temperature-controlling instrument. The reactor has no pressure controlling equipment, and the pressure in reactor was produced by the reactant thermal expansion in high temperature. The reactor pressure was measured by a pressure gage connected to the reactor. The gas inlet and outlet of the reactor was set in the cover, and also the thermocouple and pressure gage.

The experimental operation procedure is shown in Fig. 1. Reaction materials including coal tar, catalyst (4% of coal tar), and gasoline (0.5-1.5 of coal tar) were fed into the reactor, which was then sealed, evacuated, and left to equilibrate for 15 min. Hydrogen (0.03-0.08 of coal tar) was introduced into the reactor before it was heated to the desired temperature (360-400 °C, at this temperature, the pressure of reactor was 4.5-5.0 MPa), maintained at this temperature for a certain time (5-40 min), and then cooled. After the reactor was cooled to ambient temperature, it was opened and the solid, liquid, and gaseous products were separated.

The liquid product was distilled under ambient pressure to obtain the gasoline and diesel fractions directly. The distillate fraction boiling below 200 °C was the gasoline fraction, while the distillate fraction boiling in the range 200-350 °C was the diesel fraction. The light oil was the sum of the diesel and gasoline fractions. The coke was the product of condensation reaction. All product yields are specified on weight basis, and the gasoline yield is the net increase.

RESULTS AND DISCUSSION

1. Model Establishments

Coal tar hydrocracking reaction was divided into cracking and condensation reaction according to reaction properties, so the reaction network included three lumps: coal tar, gas and distillate oil, and coke. The reaction network is shown in Fig. 2.

In Fig. 2 the y_1 represents the gas and distillate oil yields, which were from the cracking reaction. The y_2 represented the coke yield, which was from the condensation reaction.

The reaction order of cracking reaction was assumed as n_1, and its reaction rate constant was K_1; the reaction order of condensa-
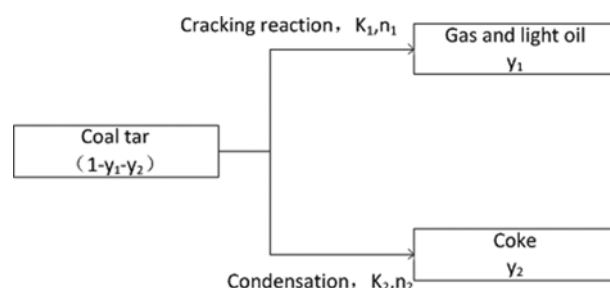

Fig. 2. Reaction network of low temperature coal tar hydrocracking in supercritical gasoline.

tion reaction was assumed as n_2, and its reaction rate constant was K_2; the reaction order of total reaction was assumed as n_3, and its reaction rate constant was K_3. The differential equation of reaction kinetics is shown in Eq. (1).

$$\frac{dy_i}{dt} = K_i \left(1 - \sum_{j=1}^{2} y_j\right)^{n_i} \quad i=1, 2, 3 \tag{1}$$

In Eq. (1), y_i represents the product yields of cracking, condensation and total reactions at residence time t; t represents the residence time, min; K_i is the reaction rate constants of cracking, condensation and total reactions, min^{-1}.

The cracking and total reactions were assumed to both be first-order reactions, and the condensation was second-order reaction; thus Eq. (2) was obtained after Eq. (1) simplification.

$$\frac{dy_1}{dt} = K_1 \left(1 - \sum_{j=1}^{2} y_j\right)$$
$$\frac{dy_2}{dt} = K_2 \left(1 - \sum_{j=1}^{2} y_j\right)^2 \tag{2}$$
$$\frac{dy_3}{dt} = K_3 \left(1 - \sum_{j=1}^{2} y_j\right)$$

P the hydrogen to represents coal tar ratio, and δ was represents the gasoline to coal tar ratio. In our experimental conditions it is assumed that the effects of P and δ on the reaction rate constant K_i could be expressed by Eq. (3).

$$K_i = k_i P^{a_i} (1+\delta)^{\lambda_i} \phi \quad i=1, 2, 3 \tag{3}$$

In which, k_i are the apparent rate constants of cracking, condensation, and total reactions, min^{-1}; a_i represents the indexes of hydrogen to coal tar ratio in cracking, condensation and total reactions. λ_i is the indexes of gasoline to coal tar ratio in cracking, condensation and total reactions. Φ is the deactivation function of catalyst, and in our experimental conditions fresh catalysts was used in every experiment, so the deactivation function of catalyst could be a constant and ϕ was equal to 1.

The effect of reaction temperature to the apparent rate constant could be expressed by the Arrhenius Equation, as shown in Eq. (4).

$$k_i = A_i e^{-\frac{E_i}{RT}} \quad i=1, 2, 3 \tag{4}$$

In which A_i is the pre-exponential factor of cracking, condensation and total reactions, E_i is the activation energy of cracking, condensation and total reactions, KJ/mol.

2. Solution of Kinetic Parameters

2-1. Solution of K_i

The effects of residence time $t_i (i=0, 1, \cdots)$ on the yields of cracking reaction (y_{1j}, j=0, 1$\cdots$), the yields of condensation reaction (y_{2j}, j=0, 1$\cdots$), and the yields of total reaction (y_{3j}, j=0, 1$\cdots$) at different operating parameters were regressed to polynomials, as shown in Eq. (5). By regression, the coefficients of the polynomials were obtained and expressed by C_{ij} (C_{ij}, i=1, 2, 3; j=0, 1$\cdots$).

$$y_i = \sum_{j=0}^{3} c_{ij} t^i \quad i=1, 2, 3 \tag{5}$$

Eq. (5) was differentiated to Eq. (6):

$$\frac{dy_i}{dt} = \sum_{j=0}^{3} j C_{ij} t^{j-1} \tag{6}$$

The values of $(dy_i/dt)_j$ (i=1, 2, 3; j=0, 1$\cdots$) at different t_i were calculated by Eq. (6) and the C_{ij}(i=1, 2, 3; j=0, 1$\cdots$). The values of $(1-\sum_{1}^{2} y_i)_j^{n_i}$ (j=0, 1$\cdots$; $n_1=1$, $n_1=2$, $n_3=1$) were calculated by the values of y_i (i=1, 2, 3) at different t_i (i=0, 1, $\cdots$). Then the values of K_i were calculated by the value of $(1-\sum_{1}^{2} y_i)^{n_i}$ and $(dy_i/dt)_j$ by Eq. (2). The effects of operating parameters to K_i are shown in Fig. 3-5.
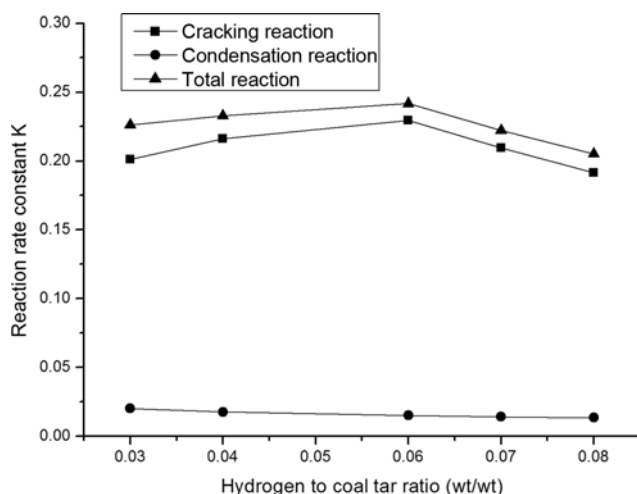

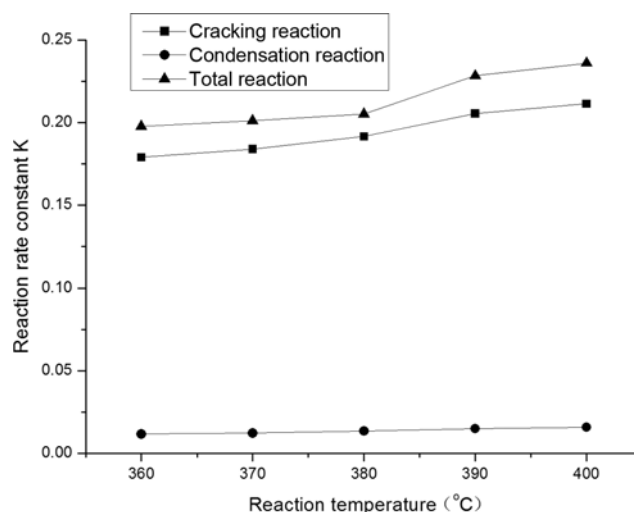**Fig. 3. The effects of hydrogen to coal tar ratio on reaction rate constants K_i.**

Fig. 4. The effects of reaction temperature on reaction rate constants K_i.

The selectivity of cracking reaction could be expressed by the value of K_1/K_2. Fig. 3 shows the relation of K_1, K_2, K_3, and K_1/K_2 with hydrogen to coal tar ratio. In Fig. 3 the values of K_1, K_3, and K_1/K_2 increased with hydrogen to coal tar ratio, reached the maximum at hydrogen to coal tar ratio of 0.06, and then started to decrease. However, the values of K_2 always decreased with hydrogen-to-coal tar ratio. The results show that more hydrogen could promote hydrogenation, inhibit coke formation, and increase the cracking reaction rate of the raw materials, resulting in a promotion of the reaction extent and K_1. However, the reactor has no pressure controlling equipment, and the pressure in reactor was produced by the reaction and materials thermal expansion in high temperature. Excessive hydrogen will increase the hydrogen partial pressure, which would decrease dissolving capacity of supercritical gasoline for coke precursors [13,14], leading to increase of condensation and reduction in K_1.

Fig. 4 shows the relation of K_1, K_2, K_3, and K_1/K_2 with temperature. In Fig. 4 the values of K_1, K_2, K_3 always increased with temperature, but the values of K_1/K_2 decreased with temperature. At higher temperature, the higher value of K_1 indicates higher cracking reaction rate, while K_1/K_2 was lower at the same time. At lower temperature, the higher value of K_1/K_2 indicates higher selectivity of cracking reaction, while the K_1 was lower at the same time. The reason may be explained as follows. Since the reaction pressure varied nearby the critical pressure of gasoline with temperature, the solubility of coal tar in supercritical gasoline decreased at higher temperature and the gasoline solvent could not adequately dissolve the coke precursors, which resulted in increase of the condensation rate and decrease of the K_1/K_2. So there exists a proper temperature at which the cracking reaction accelerated and selectivity of cracking reaction was higher.

Fig. 5 shows the relation of K_1, K_2, K_3, and K_1/K_2 with gasoline-to-coal tar ratio. In Fig. 5 the values of K_1, K_3, and K_1/K_2 increased with gasoline-to-coal tar ratio, reached the maximum at gasoline-to-coal tar ratio of 1, and then started to decrease. However the values of K_2 always decreased with gasoline-to-coal tar ratio. The results show less gasoline solvent could not adequately dissolve coal tar,
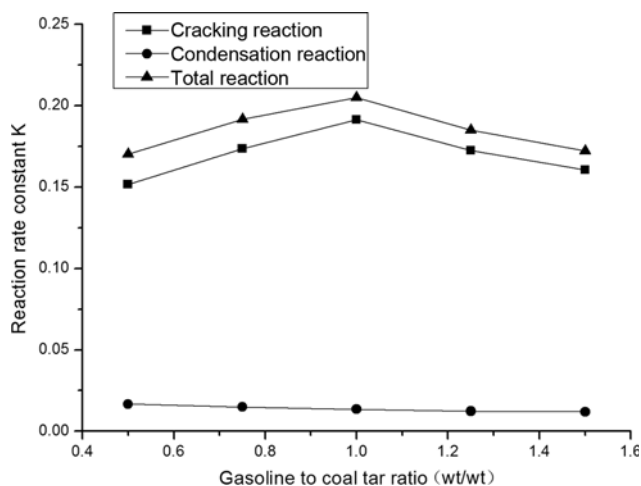
Fig. 5. The effects of gasoline to coal tar ratio on reaction velocity constants K_i.

and part of the coal tar was thermal cracked in fact, which decreased the K_1 and promoted the K_2, so the K_1/K_2 was low. With the gasoline solvent increased, coal tar was fully dissolved in the solvent, so the K_1 and the K_1/K_2 reached a maximum. However, excessive gasoline solvent reduced the concentration of reactants, resulting in decreases in the cracking and condensation rate, which resulted in the decreases of K_1, K_2, K_3, and K_1/K_2. Therefore, ascertaining the optimal ratio of gasoline solvent-to-coal tar is important to obtaining more light fractions and little coke.

2-2. Solution of Indexes of Gasoline to Coal Tar Ratio
Eq. (7) was obtained after taking the logarithm of Eq. (3), as follows:

$$\ln K_i = \ln[k_i(1+\delta)^{\lambda_i}] + a_i \ln P \quad i=1, 2, 3 \tag{7}$$

It can be seen in Eq. (7) that (i=1, 2, 3) was linear with lnP; the coefficients of one degree term were the indexes of hydrogen to coal tar ratio (a_i, i=1, 2, 3) of cracking, condensation and total reactions, so the a_i could be solved by linear regression, as shown in Table 2.

2-3. Solution of Indexes of Gasoline to Coal Tar Ratio
Eq. (8) was obtained after taking the logarithm of Eq. (3), as shown in the following:

It can be found in Eq. (8) that (i=1, 2, 3) was linear with ln(1+δ), The coefficients of one degree term were the indexes of gasoline to coal tar ratio (λ_i, i=1, 2, 3) of cracking, condensation and total reactions, so the λ_i could be solved by linear regression, as shown in Table 2.

$$\ln K_i = \ln(k_i P^{a_i}) + \lambda_i \ln(1+\delta) \quad i=1, 2, 3 \tag{8}$$

2-4. Solution of Pre-exponential Factor and Activation Energy
Eq. (9) could be obtained with Eq. (8) and Eq. (3).

$$K_i = A_i P^{a_i}(1+\delta)^{\lambda_i} e^{-\frac{E_i}{RT}} \quad i=1, 2, 3 \tag{9}$$

Eq. (10) was obtained after taking the logarithm of Eq. (9), as follows:

$$\ln K_i = \ln[A_i P^{a_i}(1+\delta)^{\lambda_i}] + \frac{-E_i}{RT} \tag{10}$$

It can be observed in Eq. (10) that $\ln K_i$ (i=1, 2, 3) was linear with 1/T. The coefficients of one degree term were ($-E_i$)/R (i=1, 2, 3) and the constant term was $\ln[A_i P^{a_i}(1+d)^{\lambda}]$, which could be solved by linear regression, as shown in Table 2. The activation energies (E_i, i=1, 2, 3) and pre-exponential factors (A_i, i=1, 2, 3) of cracking, condensation and total reactions could be calculated with the known R, P, a_i, δ, and λ, also as shown in Table 2.

Table 2 shows the kinetic constants of cracking, condensation and total reactions during low temperature coal tar hydrocracking in supercritical gasoline.

2-5. Kinetic Model
Through model establishment and solution of the kinetic constants, the kinetic models during low temperature coal tar hydrocracking in supercritical gasoline are shown in Eq. (11)-(13).

$$\frac{dy_1}{dt} = 0.4685e^{-\frac{1883.5}{T}} P^{-0.6297}(1+\delta)^{0.3802}\left(1-\sum_{j=1}^{2} y_j\right) \tag{11}$$

$$\frac{dy_2}{dt} = 1.4451e^{-\frac{3429.5}{T}} P^{-0.4082}(1+\delta)^{-0.6806}\left(1-\sum_{j=1}^{2} y_j\right)^2 \tag{12}$$

$$\frac{dy_3}{dt} = 0.8303e^{-\frac{2037.7}{T}} P^{-0.5717}(1+\delta)^{0.1903}\left(1-\sum_{j=1}^{2} y_j\right) \tag{13}$$

Table 2. Dynamics constants of low temperature coal tar hydrocracking in supercritical gasoline

Dynamics parameter		Unit	Cracking		Condensation		Total reaction	
			Value	R	Value	R	Value	R
Index of hydrogen to coal tar ratio	a_i	-	−0.6297	0.8648	−0.4082	0.9960	−0.5717	0.9942
Index of gasoline to coal tar ratio	λ_i	-	0.3802	0.8987	−0.6806	0.9919	0.1903	0.8362
Activation energy	E_i	KJ·mol^{-1}	15.6553	0.9738	28.5129	0.9852	16.9414	0.8978
Pre-exponential factor	A_i	min^{-1}	0.4685	0.9365	1.4451	0.9546	0.8303	0.9286

Table 3. Comparison of calculated and trial values

Item	y_1	y_2	y_3	K_1	K_2	K_3	dy_1/dt	dy_2/dt	dy_3/dt
Trial value	0.6784	0.0426	0.7210	0.2296	0.0151	0.2418	0.0641	0.0012	0.0675
Calculated value	0.6743	0.0421	0.7164	0.2285	0.0148	0.2409	0.0648	0.0012	0.0683

2-6. Model Validation

To verify the kinetic model, the calculated and trial values were compared, as shown in Table 3. The trial value was obtained at the conditions of hydrogen to coal tar 0.06, reaction temperature 380 °C, gasoline to coal tar ratio 1, and residence time 20 min. The results show that the calculated values and trial values coincided; the kinetic models could better explain the reaction rules of low temperature coal tar hydrocracking in supercritical gasoline.

CONCLUSIONS

Kinetic models of low temperature coal tar hydrocracking in supercritical gasoline was established; the kinetic parameters, including reaction rate constant, activation energy, and pre-exponential factor, were obtained through the regression of experiment data. It was verified that the proposed model could better interpret the variation law of kinetic constants and operating parameters, including hydrogen-to-coal tar ratio, gasoline-to-coal tar ratio, reaction temperature, and residence time. The proposed model could not only predict the yields successfully, but also provide proper operating parameters to reduce the coke content and to enhance the coal tar conversion to light fractions.

REFERENCES

1. T. Kan, H. Y. Wang, H. X. He, C. Li and S. Zhang, *Fuel*, **90**, 3404 (2011).
2. Z. J. Shi, M. X. Fang, C. G. Zhou, S. R. Wang and Z. Y. Luo, *Adv. Mater. Res.*, **673**, 347 (2012).
3. Y. Liu, F. Bai, C. C. Zhu, P. Q. Yuan, Z. M. Cheng and W. K. Yuan, *Fuel Process. Technol.*, **106**, 281 (2013).
4. J. Long, B. X. Shen, H. Ling, J. Zhao and J. Lu, *Ind. Eng. Chem. Res.*, **50**, 11259 (2011).
5. L. N. Han, R. Zhang and J. C. Bi, *J. Anal. Appl. Pyrol.*, **91**, 281 (2011).
6. B. L. Dou, W. G. Pan, J. X. Ren, B. B. Chen, J. Hwangb and T. U. Yu, *Energy Convers. Manage.*, **49**, 2247 (2008).
7. J. Yang, X. G. Wang, L. Li, S. Kui, X. G. Lu and W. Z. Ding, *Appl. Catal. B: Environ.*, **96**, 232 (2010).
8. L. N. Han, R. Zhang and J. C. Bi, *Fuel Process. Technol.*, **90**, 292 (2009).
9. C. X. Ma, R. Zhang and J. C. Bi, *J. Fuel Chem. Technol. (Chin)*, **31**, 401 (2003).
10. S. X. Wang. *Petroleum refinery engineering* (in Chinese), Petroleum Industry Press, Beijing (1988).
11. Z. L. Gu, N. Chang, X. P. Hou, J. P. Wang and Z. K. Liu, *Fuel*, **91**, 33 (2012).
12. N. Chang, Z. L. Gu, Z. S. Wang, Z. K. Liu, X. P. Hou and J. P. Wang, *J. Porous Mater.*, **18**, 589 (2010).
13. H. S. Van den and M. Harrod, *Ind. Eng. Chem. Res.*, **40**, 5052 (2001).
14. M. G. Hitzler, F. R. Smail, S.K. Ross and M. Poliakoff, *Org. Process. Res. Dev.*, **2**, 137 (1998).