



Reaction pathway analysis in thermal cracking of waste cooking oil to hydrocarbons based on monomolecular lumped kinetics



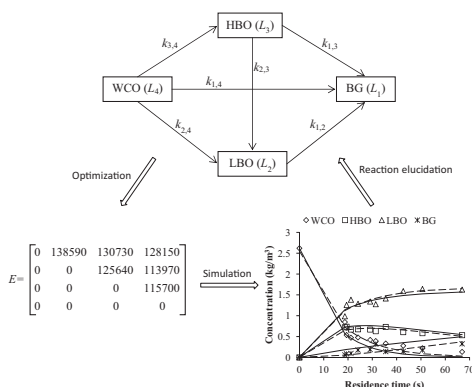
Balasubramanian Periyasamy*

Chemical Engineering, Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak Campus, 93350 Kuching, Sarawak, Malaysia

HIGHLIGHTS

- A kinetic model was presented for thermal cracking of waste cooking oil.
- Activation energy was estimated through hybrid optimization.
- All parallel reactions from waste cooking oil are dominant.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 March 2015
 Received in revised form 18 May 2015
 Accepted 27 May 2015
 Available online 3 June 2015

Keywords:

Triglycerides
 Thermal cracking
 Discrete lumping
 Kinetics
 Hybrid optimization
 Activation energy

ABSTRACT

This article presents a comprehensive kinetic model for thermal cracking of waste cooking oil using monomolecular lumped kinetics. The chemical lumps were classified on the basis of carbon number range of the hydrocarbons and a first order irreversible monomolecular cracking kinetics was considered for finding the product concentration in a reactor. Arrhenius kinetic law was applied for determining temperature dependency of the apparent kinetic constants included in the model. The parameter reduction was performed by calculating the preexponential factors through transition state theory and statistical thermodynamics concepts. The activation energy of the reactions was estimated through hybrid optimization using experimental data available in the literature. The proposed kinetic model for thermal cracking of waste cooking oil exhibits good agreement with the experimental data. Furthermore, the present kinetic analysis reveals that all parallel reactions from waste cooking oil are dominant for producing hydrocarbons in a product lump as compared to reactions in series and further cracking of product lumps.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Vegetable oil is a renewable feedstock currently being used for production of green fuels through various technologies such as thermal cracking, catalytic cracking and hydrocracking [1–4]. Green fuels are used as an alternative for petroleum fuels as a

result of depletion of crude oil reserves and have similar properties as that of petroleum fuels. The primary constituent is triglycerides in all vegetable oils. The conversion of triglycerides into green fuels was received considerable attention worldwide for incorporation of co-processing of triglycerides along with the existing refinery processes such as thermal cracking, catalytic cracking, and hydroprocessing [2–4]. Non-edible and waste cooking oils [5] can be used as raw materials for the green conversion processes. Jatropha [6] and rubber seed [7] oils are the typical examples of

* Tel.: +60 82260842; fax: +60 82260813.

E-mail address: bperiyasamy@swinburne.edu.my

Nomenclature

$A_{j,i}$	preexponential factor for the formation of a product in lump L_j from reactant lump L_i (s^{-1})	N_A	Avogadro's number ($=6.023 \times 10^{23} \text{ mol}^{-1}$)
c_{exp}	experimental data	N_L	number of lumps
c_L	vector of concentration of reacting species in each lump (kg m^{-3})	NQ	number of responses
\dot{c}_L	vector of time-derivatives of concentration of reacting species in each lump	r_{L_i}	rate of reaction for the thermal cracking reactions in lump L_i ($\text{kg m}^{-3} \text{ s}^{-1}$)
c_{L_i}	concentration of reacting species in lump L_i (kg m^{-3})	R	gas constant ($=8.314 \text{ J mol}^{-1} \text{ K}$)
c_{model}	model calculated data using Eq. (10)	T	temperature (K)
$E_{j,i}$	activation energy for the formation of a product in lump L_j from reactant lump L_i (J mol^{-1})	t	residence time (s)
L_i	label of a lump	S_{tr}°	absolute translational entropy of a molecule ($\text{J mol}^{-1} \text{ K}^{-1}$)
$k_{j,i}$	apparent kinetic constant for the formation of a product in lump L_j from reactant lump L_i (s^{-1})	V_m	molar volume of a molecule ($\text{m}^3 \text{ mol}^{-1}$)
k_B	Boltzmann constant ($=1.38065 \times 10^{-23} \text{ J K}^{-1}$)	$w_{j,r}$	inverse of elements of variance-covariance matrix of experimental errors
h	Planck constant ($=6.62607 \times 10^{-34} \text{ J s}$)		
M_w	molecular weight of a molecule		
N	number of observations		
		<i>Greek symbols</i>	
		$\Delta S^{\ddagger \neq}$	change in standard entropy of a lump at transition state ($\text{J mol}^{-1} \text{ K}^{-1}$)
		ΔH	change in standard enthalpy of a lump (J mol^{-1})

non-edible oils [8] and contain a mixture of triglycerides, diglycerides, monoglycerides and free fatty acids [9]. This mixture can be converted into useful hydrocarbons through hydrodeoxygenation, decarboxylation, decarbonylation and thermal cracking reactions [6,9].

In the literature, kinetic experiments were performed for thermal cracking of vegetable oils such as canola [10–13], soybean [13,14], rapeseed [15], and buriti [16] oils. In addition, thermal cracking of Calotropis procera biocrude [17], oleic acid [18], abietic acid and tall oil fatty acids [19] was also studied. The free radical chemistry for thermal cracking of triglycerides to hydrocarbons was proposed by several researchers [10,12,16,20–23]. The plausible free radical reactions considered are breaking of C–O bonds present at the backbone of the triglycerides followed by decarbonylation, decarboxylation, ketene elimination, β -scission, alkylation, cyclization, aromatization and so on. However, the detailed kinetic model for thermal cracking of triglycerides was not reported. Recently, the vacuum pyrolysis experiments for the conversion of plant oil asphalt to hydrocarbons were performed and five lump kinetic model was developed by Zheng et al. [24]. The catalytic hydrodeoxygenation [25–30] of vegetable oils to diesel and gasoline range hydrocarbons was investigated, and optimal operating conditions and a catalyst for the process were identified. Although researcher performed the kinetic experiments for conversion of vegetable oils through hydrodeoxygenation, decarbonylation, decarboxylation and thermal cracking, the kinetic modeling of these processes was not well established.

Kinetic modeling is indispensable for process development in the conversion of vegetable oils to market-driven transportation green fuels. The kinetic modeling of refinery processes such as thermal cracking [31–37], catalytic cracking [38–44] and hydrocracking [45–52] was well established. Discrete lumping approach [31–49,52] was successfully applied for modeling of aforementioned processes. Thermal cracking of residual feedstock was investigated in a batch reactor and observed that the reactions follow first order kinetics [31]. A kinetic model for thermal cracking reactions in bitumen reservoirs was developed by Jia et al. [32]. Thermal cracking of kerosene for producing ethylene and propylene was studied in a tubular reactor and a semi-mechanistic model was developed for determining the yield of products [33]. Sundaram and Froment [34] developed molecular reaction schemes for thermal cracking of ethane, propane and their mixtures from observed product distribution, radical mechanisms

and thermodynamic properties. Thermal cracking of gas oil was experimentally studied in a pilot plant tubular reactor and a fundamental kinetic model was developed for determining the product distribution in a thermal cracker unit [35]. Kinetic models for thermal cracking of vacuum residues in the Eureka process were developed using monomolecular [36] and binary [37] cracking kinetics.

Recently, the kinetic experiments for thermal cracking of waste cooking oil were performed in a pilot plant tubular reactor by Meier et al. [53]. A four lump model was developed for the conversion of waste cooking oil to heavy bio-oil, light bio-oil and bio-gas using monomolecular lumped cracking kinetics. The kinetic constants included in the model were estimated through unweighed regression at each reaction temperature. However, they assumed that the bio-gas was produced only from thermal cracking of light bio-oil in the model.

The thermal cracking of waste cooking oil undergoes breaking of C–O bonds present at the backbone of triglycerides for producing monoglycerides and C_3 hydrocarbons (acrolein, ethylene, CO and CO_2) in the heavy bio-oil and bio-gas, respectively. Subsequently, the monoglycerides may undergo C–C bond breaking mainly at positions β to C=C bonds, decarbonylation and decarboxylation reactions for producing low carbon number range hydrocarbons in the light bio-oil and less than C_4 hydrocarbons in the bio-gas. Thus, the possibility for the formation of bio-gas from waste cooking oil and heavy bio-oil should be considered in the reaction stoichiometry in addition to thermal cracking of light bio-oil to bio-gas. Therefore, a comprehensive discrete lumped kinetic model for thermal cracking of waste cooking oil was developed and model adequacy was evaluated using experimental data available elsewhere [53].

2. Kinetic modeling

In the following, a kinetic model for thermal cracking of waste cooking oil to hydrocarbons based on monomolecular lumped reactions is presented.

Recently, Meier et al. [53] developed a model for thermal cracking of WCO based on monomolecular lumped kinetics over the range of temperatures 748–798 K. The lumps were classified on the basis of carbon number range of the hydrocarbons [53] and are illustrated in Table 1. The lumped cracking reactions presented by Meier et al. [53] is

Download English Version:

<https://daneshyari.com/en/article/6635029>

Download Persian Version:

<https://daneshyari.com/article/6635029>

[Daneshyari.com](https://daneshyari.com)