

SCIENCE | ENGINEERING | TECHNOLOGY

e-ISSN: 2319-8753 | p-ISSN: 2347-6710

EDIA

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 10, October 2021

INTERNATIONAL STANDARD SERIAL NUMBER INDIA

Impact Factor: 7.569

9940 572 462

6381 907 438

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e-ISSN: 2319-8753, p-ISSN: 2347-6710 www.ijirset.com | Impact Factor: 7.569



Volume 10, Issue 10, October 2021

DOI:10.15680/IJIRSET.2021.1010057

Transesterification of Waste Cooking Oil: Kinetic Study and Reactive Flow Analysis

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ABSTRACT: Homogenous catalyst transesterification of biofuel into a biodiesel is a multiple, reversible reactions process. It is steered by several parameters including residence time, the reactants quality, proportions, state of mixing, as well as catalyst amount and temperature. In this work the chemical kinetics of a simple and robust tubular semi-continuous reactor of methoxide and biomass lipid is carried out in the presence of NaOH (sodium hydroxide) homogenous catalyst. The kinetic parameters are evaluated for the mixed waste cooking oil (WCO). Results demonstrated that higher conversion and product yield is achieved at relatively higher temperatures and methanol to triglyceride molar ratios, and longer residence time. The kinetic study is carried out at the optimal conversion metrics. The obtained kinetic data was found to be in line with the published kinetic studies and inferior to published data for virgin oil under the similar process parameters. The evaluated rate constants and their activation energies are implemented in high fidelity reactive flow simulation and resulted in a worthy reaction trend that brought more insight to several reactor and flow parameters.

KEYWORDS: Transesterification; chemical kinetics; reactive flow; waste oil processing.

I. INTRODUCTION

While the quest of finding non-conventional and renewable energy resources seems challenging, development of safe inexpensive waste management processes is an even greater one. Recovery and recycling of waste materials is a dual solution to this pursuit. The waste oil of the trapped grease, lard, and used cooking oil can be collected and converted into a suitable grade of Biodiesel as methyl or ethyl ester via transesterification process. Results obtained by our group [1] and elsewhere [7] demonstrated the efficiency and lower combustion emission of this biodiesel substitute in Internal Combustion Engines.

Biodiesel, if efficiently produced, is a near carbon neutral resource which emits lower hydrocarbon when burnt. Algae oil and waste cooking oil have come into limelight when considering the constraints of using farmland for energy production; the use of waste cooking oil is another important resource for biodiesel production. Results confirm that there is a massive amount of waste cooking oil with unsatisfactory disposal practices ranging from the inefficient use as a saponification agent to improper drainage flushing. The Energy Information Administration in the United States estimated that around 100 million gallons of waste cooking oil is produced per day in USA, where the average per capita waste cooking oil is 9 pounds. The estimated amount of waste cooking oil collected in Europe is about 700,000 - 100,000 tons/year [2]. This oil source additional to non-edible oil and animal fat can be converted to methyl or ethyl ester by transesterification. This is not only a sustainable energy source in developing societies, but also an effective way to address waste management concerns.

In this work, used cooking oil is transesterified using homogenous NaOH catalyst at optimal conditions. Kinetic study is carried out to estimate the rate constants of the three, reversible, step chemical reactions as well as the overall transesterification reactions of the triglycerides into FAME, glycerol, and their intermediates. The obtained kinetic data is an important move for gaining insight to the distribution and reactivity of the mixture as well as the development of a predictive reactive flow model. The developed model enables the analyst to a study a long list of process parameters including:reactant molar ratio, temperature, residence time, reactor configuration etc.

II. MATERIALS AND METHOD

Different waste cooking oil samples were collected from popular restaurant chains and the Masdar campus cafeteria. The sunflower branded oil is the most commonly used oil in the region; at a daily rate of 750 to 900 meals the average WCO weekly generation is near 100liters. The samples are collected in a large stainless-steel container (150liter

International Journal of Innovative Research in Science, Engineering and Technology (IJIRSET)

| e-ISSN: 2319-8753, p-ISSN: 2347-6710| <u>www.ijirset.com</u> | Impact Factor: 7.569|

Volume 10, Issue 10, October 2021

DOI:10.15680/IJIRSET.2021.1010057

capacity), then subjected to sun heating reaching near 45oC for easy filtering. The test samples are filtered using 20µm paper filter leaving behind suspended solid residuals. It is then dried using a magnetic stirring heating pad set at 100oC and 250rpm in preparation for methoxide mixing. High purity GCMS 99.99% grade methanol is used for all the experiments. NaOH, Sigma-Aldrich tablets were then solubilized in methanol using a similar heating and stirring pad at the designated proportion forming a homogeneous methoxide solute. The water free WCO is first titrated using phenolphthalein and then an appropriate amount of NaOH is used to neutralize it. Agilent dissolution apparatus is used as a multiple of eight reactors to arrive to the optimal parameters.

Kinetic study: It is carried out in the tubular reactor which is connected to two reservoirs in a closed and continuous flowing cycle. The reactor consists of two concentric upright cylinders chambers. Detailed drawings of the chambers and their exact dimensions are found elsewhere of the authors' work [4]. The flow is steered by a single peristaltic pump entering the reactor chamber, beyond turbulent limit which stipulates well-stirred flow conditions. The flow enters and exits the reactor chambers circumferentially and is inducted helically to lengthen the residence time, thereby having better reaction rate and yield. At the reactor's exit samples are collected in 10mm vials and refrigerated to freeze their reactivity for later analysis. The analysis of the sample composition as far as Triglyceride (TG), Diglyceride (DG), Monoglyceride (MG), Ester/FAME (E) and Glycerol (GL) is carried out using Thermoscientific DSQ 6000 GC/MS equipped with an FID column. Multiple repetitions (at least three) of fifteen reaction time steps was obtained covering the two-hour reaction time. The procedures of obtaining the breakup of the sample composition of Triglyceride, Monoglyceride, and Alcohol (AL) are those carried out by Nourieddine et al. [2] and Janajreh [4]. The transesterification conversion is represented by the three reversible elementary reactions additional to a forth shunt/overall reaction and are written as:

TG+AL	 E+DG	(1)
DG+AL MG+AL	 E+MG E+GL	(2) (3)
TG+3AL	 3E+GL	(4)

They are mathematically represented by six coupled partial differential equations (PDE's) of a 1s^t order derivative and are written as:

 $dTG/dt = -K1[TG][AL] + K2[E][DG] - K7[TG][AL]^3 + K8[E]^3[GL] (5)$

dDG/dt = -K3 [DG] [AL] + K4 [E] [MG] + K1 [TG] [AL] - K2 [E] [DG] (6)

dMG/dt = -K5 [MG] [AL] + K6 [E] [GL] + K3 [DG] [AL] - K4 [E] [MG] (7)

dE/dt = K1 [TG] [AL] - K2 [E] [DG] + K3 [DG] [AL] - K4 [E] [MG] + K5 [MG] [AL] - K6 [E] [GL] + K7 [TG] [AL]3- K8[E]³ [GL](8)

dGL/dt = K5 [MG] [AL] - K6 [E] [GL] + K7 [TG] [AL]³ - K8 [E]³[GL] (9)

dAL/dt = -dE/dt(10)

The above system is solved for K1 through K8 at minimum *RMS* following the temporal measurements of each species according to A x = b or $x = A^{-1}b$. Where A is the coefficient matrix of the concentrations at each time step and x is the rate constant vector, i.e., K1 through K8; and b is given by time differencing of the measured concentrations. The rate constant of each of the eight reactions is expressed as:

$$K = K e^{-E/RT}$$
 or $\ln K = \ln K - E1(11)$
R T

Where Ko is the pre-constant, E is the activation energy, R is the universal gas constant and T is the reaction temperature in Kelvin degree. Therefore, from the slope of the natural log of K vs 1/T one can determine the activation energy in J/mole, whereas the intercept of that line is the natural log of the reaction pre-constant Ko.

Reactive flow: The evaluated kinetic data is implemented in high fidelity reactive flow model following the author's previous work [4]. This is carried out in a tubular reactor which consists of two coincided and separated chambers

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Volume 10, Issue 10, October 2021

DOI:10.15680/IJIRSET.2021.1010057

that brings many features including compactness, low pressure drop, ease of temperature control and near isothermal conditions additional to the modularity for easy scale up/down. The reactants are introduced circumferentially and hence minimizing the pressure drop and increasing the residence flow time by following a swirling trajectory. The modularity can be achieved through multiple reactor stack or simply using longer fittings. The continuity, momentum, transport species, and turbulence scalars are solved iteratively within the framework of Ansys Fluent [16] for the discretized reactor geometry (12cm radius 30cm height). The developed predictive computational fluid model enables the analyst to carry out different parametrical study to arrive to optimal conversion metrics by adjusting the flow conditions and the reactor configuration.

III. RESULTS AND DISCUSSION

Kinetic study: The evaluated GC/MS along with the evaluated rate constants are depicted in Fig.1. Results of the activation energy in comparison to those obtained in the literature are summarized in Table 1. It appears that the corresponding reaction rate constant values are within the same order of magnitude as of the work of Noureddini and Zhu [2]. Their work however considered virgin soybean oil that has been demonstrating good conversion behaviour compared to other virgin oils (i.e. sunflower an palm oil). The order of magnitude of the evaluated activation energy however is comparable for the TG and DG reactions but at much higher value for the MG reactions. Both DG and MG are short lived species as they appear and asymptotically disappear. The amount of remaining methanol is nearly equal to the excess amount, suggesting a good level of reactivity of the TG. The activation energy is dominated by the forward shunt reaction and is the least for the forward TG reaction. It is worth to emphasize that the adopted kinetic reaction model of these inferred values is a pseudo first-order and is combined with shunt reversible reaction scheme. It is a similar model to that used in the work of Freedman and co-workers [14]. The main assumption of the simulation is the homogenization of the two reactants at the reactor inlet. This enables one to model the flow as a single phase of multiple species mixture. Therefore, the state of mixedness or the introduction and or promoting flow turbulence through the operating conditions or reactor configuration is a key behind the validity of this assumption.



Fig. 1. WCO chemical kinetic results from the conversion at 50 oC and 60 oC and corresponding reaction rates values $(TG\leftrightarrow DG, DG\leftrightarrow MG, MG\leftrightarrow GL, TG+3AL\leftrightarrow 3E+GL)$

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Reaction	K1	K2	K3	K4	K5	K6	K7	K8
constant								
WCO at 50OC*	0.003	0.13	0.07	0.26	0.096	0.001	1.1E-8	0.0033
5		33	52	99	3	6		
WCO at 60OC*	0.034	0.09	0.08	0.27	0.114	0.003	2.1E-8	0.0027
7		57	20	22	3	5		
Noureddini Zhu	0.049	0.10	0.21	1.28	0.239	0.007	7.84E-	1.58E-
[2]		2	8	0			5	5
Act. Eng. kJ/	E1	E2	E3	E4	E5	E6	E7	E8
kmol								
WCO at 50-60	2107.	2908	7508	4080	15,06	70,39	282,09	166,29
⁰ C*	45	.0	.8	.4	2.2	5.7	15	9.4
Noureddini Zhu	2419.	1827	3655	2694	1181.	1764.	-	-
[2]	2	9	1	2	72	6		

Table 1. Reaction measured rate constant and activation energy compared to those obtained in the literature [9].

Reactive flow: A hybrid hexagon is generated comprised of 27,500 cells for the two chambers and the connecting tubing. Mixture of the AL and TG species are introduced circumferentially, the upright reactor at Re 6,000 (based on the bottom inlet diameter of 4mm) and T=50oC into the inner reactor chamber and at different AL/TG molar ratio. Atmospheric pressure outlet boundary condition is assigned at the outer tube chamber located at the top. The no slip wall conditions are imposed at the reactor surfaces. Description of the six species are summarized in Table 2. A steady state solution is sought for the flow which enters the reactor by means of an external peristaltic pump at an adjustable flow rate of 50 to 1,000ml/min.

Table 2. Summary of specie	es properties and l	MW			
Species	Chemical formula	Molecul ar weight	Viscosity (kg/m.s)	Cp (J/ kg.oC)	Dens ity Kg/ m3
Methanol	CH4O	32	3.96E -4	1.470E3	791.8
Waste oil/ Triglyceride	${}^{C_{54}H_{105}}_{O_6}$	849	1.61E -2	2.2E3	883.3
Diglyceride	C ₃₇ H ₇₂ O 5	596	-	-	880
Monoglyceride	$\begin{array}{c} C_{20}H_{40}\\ O_4\end{array}$	344	-	-	875
Biodiesel	C ₁₈ H ₃₆ O 6	284	1.12E -3	1.187E3	870
Glycerol	C3H9O	93	1.412 E0	0238.6	1261

In this work, transesterification is attempted at two temperature values (50 oC and 60 oC) and at Re beyond the laminar regime that insures the homogeneity of the reactants. Hence, the limited mass transfer initiation stage is avoided rendering the flow as a single phase as also indicated by Boer [9]. It is to be mentioned that the total particle transfer time is nearly an order of magnitude higher than the residence time of the flow being introduced along the reactor axis. As the flow entrains in a swirl trajectory, the reactivity is enhanced. The model results at the baseline condition of 1:3 waste oil to methanol ratio are presented below in Fig. 2. At these conditions a low conversion of 40% is achieved which is attributed to the shorter residence time, a low kinetics of the reacting species, as well as lower availability of methanol.

e-ISSN: 2319-8753, p-ISSN: 2347-6710 www.ijirset.com | Impact Factor: 7.569

|| Volume 10, Issue 10, October 2021 ||

DOI:10.15680/IJIRSET.2021.1010057



Fig. 2. Molar fraction of species across the reactor (Global scale)

Results for the influence of the AL/TG ratio, inlet flow velocity and enlargement of the reactor are shown in Fig. 3. As the molar ratio is increased the rates of the forward reactions dominate the reversible reactions and more lipid conversion takes place. The velocity trend is the opposite in the same graph, as higher velocity enables more throughput, however, it reduces the residence time and consequently lower conversion occurs. The influence of the reactor extended length and width are illustrated which shows the length is more dominant compared to the enlargement of the width.



Fig. 3. Influence of molar ratio and both velocity and length and width of the reactor

V. CONCLUSION

In this work, several experiments for the transesterification of waste cooking oil were carried out using the homogeneous NaOH catalyst. Chemical kinematic study was carried out first, to evaluate the rate constants and activation energy of transesterification reactions. The molar composition of the six triglyceride, diglyceride, monoglyceride, biodiesel species including, glycerol, and alcohol was measured at different reaction times using GC/MS equipped with appropriate FAME columns and following FID methodology. The rate of reaction constants as well as their corresponding activation energies for eight elementary transesterification reactions were evaluated. Their rates appear to be near to those values obtained by Noureddine [2] for the virgin oil. The evaluated rate constants and their are implemented in high fidelity numerical simulation and resulted in a worthy activation energy reaction trend. The developed model was then subjected to different sensitivity studies including the molar rate, the inlet velocity, the size of the reactor and the inlet temperature. These results have brought more insight to the conversion rate, reaction rate, and species distribution. The conversion is in the favor of the excess amount of methanol, lower inlet velocity, and longer reactor. The former enhances the first three forward reactions while the latter enhances the residence time which also favors the asymptotic production of the biodiesel and the reduction of the intermediates (DG and MG).

International Journal of Innovative Research in Science, Engineering and Technology (IJIRSET)

e-ISSN: 2319-8753, p-ISSN: 2347-6710 www.ijirset.com | Impact Factor: 7.569



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DOI:10.15680/IJIRSET.2021.1010057

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