

# Vegetable Oil to Biofuel by Cracking: Equilibrium Product Selectivities

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**Abstract**— The equilibrium composition of biofuel formed by cracking of a modeled vegetable oil has been predicted using the system Gibbs energy minimization. In particular the effects of temperature and feed dilution by inert on the equilibrium product selectivities have been studied. Methane, aromatics and small amounts of H<sub>2</sub>, CO and CO<sub>2</sub> were predicted in the 350 – 600°C range. The increase in temperature decreases the CH<sub>4</sub>, aromatics and CO<sub>2</sub> molar proportion in the equilibrium product. Feed dilution slightly increases the carbon selectivity to CO in the 350-450°C range, decreases the carbon selectivity to CO<sub>2</sub> and has no significant effect on the carbon selectivity to CH<sub>4</sub> and aromatics.

*Index Terms*— Cracking, equilibrium product, vegetable oil

## I. INTRODUCTION

ENERGY from renewable sources is currently among the most researched topics around the globe because of the challenges that the world is facing. These challenges include high energy demand, especially in fast developing regions, depletion of fossil fuel reserves and environmental challenges such as CO<sub>2</sub> emissions which contribute to the global warming and climate change. Biofuel produced from plant-derived biomass such vegetable oils is considered “CO<sub>2</sub> neutral” since they are from plant sources which typically remove CO<sub>2</sub> from the atmosphere, and release the same amount when burnt [1]. Vegetable oils can undergo processes such as transesterification, cracking, steam reforming, etc. in order to produce biofuel. Taufiqurrahmi and Bhatia [1] have recently reviewed the catalytic cracking of edible and non-edible oils for the production of biofuels. They have indicated that catalytic cracking is one of the most efficient methods to produce biofuel, especially biogasoline, by cracking of vegetable oil in the presence of suitable catalyst.

Although various operating conditions have been reported in literature, very little is known on the equilibrium composition of the formed biofuel under different cracking conditions. This information is very useful for process

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design and development. This study aims at predicting the equilibrium composition of biofuel formed by vegetable oil cracking. In particular the effect of temperature and feed dilution by inert on the equilibrium product selectivities will be studied.

## II. METHODOLOGY

The prediction of the equilibrium product composition for vegetable oil cracking process was performed with ChemCad 6.4 simulation package. The feed to the cracking reactor was chosen as 1 kmol/h of vegetable oil without and with various degrees of dilution by an inert gas. The effect of temperature on the equilibrium product was studied in the 350 – 600°C range and oil to inert molar ratios of 1:1, 1:10 and 1:100 were used to determine the effect of feed dilution on the equilibrium product. The selected process pressure was 1 bar throughout this study. The vegetable oil was modelled by triolein and the cracking process was modelled by Gibbs free energy minimization in ChemCad. The Gibbs reactor model is based on the principal that at chemical equilibrium the total Gibbs energy of the system has its minimum value. By attempting to minimize the total energy of the system, individual equilibrium constants are not considered. Rather, the possible reaction species are noted, and the distribution of these species is established using a general mathematical technique to give a minimum free energy for the system [2]. The selected possible components in the predicted equilibrium product included H<sub>2</sub>, CO, CO<sub>2</sub>, alkanes (C<sub>1</sub> to C<sub>15</sub>), olefins (C<sub>2</sub> to C<sub>15</sub>), cyclic hydrocarbons, aromatic compounds, light ketones, alcohols, carboxylic acids and solid carbon. Except for the solid carbon, all the selected components with their physical and chemical properties were available in ChemCad 6.4 components database. The solid carbon was added to the ChemCad components database and was modelled as graphite. The graphite heat capacity polynomial coefficients determined by Butland and Maddison [3] were used in the simulation. The enthalpy and Gibbs energy of formation for the solid carbon were entered as 0 kJ/mol.

III. RESULTS AND DISCUSSION

A. *Effect of temperature*

The effect of temperature on vegetable oil cracking equilibrium product composition is summarized in table 1.

Complete conversions for triolein were predicted in the 350-600°C range and the major products were methane (56.9 to 62 mol.%) and aromatics (19.1 to 22.3 mol.%) with a combined proportion accounting for ca. 76 to 84 mol.% of the total product. The remaining proportion was mainly

TABLE I  
 VEGETABLE OIL CRACKING EQUILIBRIUM PRODUCT COMPOSITION AS FUNCTION OF TEMPERATURE

Products		Product molar composition [%]					
Components	Chemical formula	350°C	400°C	450°C	500°C	550°C	600°C
Hydrogen	(H <sub>2</sub> )	0.1112	0.2741	0.5996	1.1902	2.1743	3.6942
Carbon monoxide	(CO)	6.8394	12.9617	17.7263	19.6706	20.1752	20.2029
Carbon dioxide	(CO <sub>2</sub> )	7.8850	4.3775	1.6440	0.5001	0.1539	0.0520
Water	(H <sub>2</sub> O)	0.0061	0.0076	0.0073	0.0060	0.0047	0.0036
Triolein	(C <sub>57</sub> H <sub>104</sub> O <sub>6</sub> )						
Coke	C						
		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
<b>Alkanes</b>		<b>62.8087</b>	<b>61.5219</b>	<b>60.3259</b>	<b>59.4046</b>	<b>58.3746</b>	<b>56.9164</b>
Methane	(CH <sub>4</sub> )	62.7772	61.4885	60.2908	59.3677	58.3362	56.8771
Ethane	(C <sub>2</sub> H <sub>6</sub> )	0.0313	0.0333	0.0350	0.0367	0.0383	0.0392
N-propane	(C <sub>3</sub> H <sub>8</sub> )	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
N-butane	(C <sub>4</sub> H <sub>10</sub> )						
N-pentane	(C <sub>5</sub> H <sub>12</sub> )						
N-hexane	(C <sub>6</sub> H <sub>14</sub> )						
N-heptane	(C <sub>7</sub> H <sub>16</sub> )						
N-octane	(C <sub>8</sub> H <sub>18</sub> )						
N-nonane	(C <sub>9</sub> H <sub>20</sub> )						
N-decane	(C <sub>10</sub> H <sub>22</sub> )						
N-Undecane	(C <sub>11</sub> H <sub>24</sub> )						
N-dodecane	(C <sub>12</sub> H <sub>26</sub> )						
N-tridecane	(C <sub>13</sub> H <sub>28</sub> )						
N-tetradecane	(C <sub>14</sub> H <sub>30</sub> )						
N-pentadecane	(C <sub>15</sub> H <sub>32</sub> )						
<b>Olefins</b>		<b>0.0004</b>	<b>0.0013</b>	<b>0.0034</b>	<b>0.0083</b>	<b>0.0181</b>	<b>0.0359</b>
Ethylene	(C <sub>2</sub> H <sub>4</sub> )	0.0004	0.0012	0.0033	0.0080	0.0175	0.0348
Propylene	(C <sub>3</sub> H <sub>6</sub> )		0.0001	0.0002	0.0003	0.0006	0.0011
1-butene	(C <sub>4</sub> H <sub>8</sub> )						
1,3-butadiene	(C <sub>4</sub> H <sub>6</sub> )						
1-pentene	(C <sub>5</sub> H <sub>10</sub> )						
1-hexene	(C <sub>6</sub> H <sub>12</sub> )						
1-heptene	(C <sub>7</sub> H <sub>14</sub> )						
1-octene	(C <sub>8</sub> H <sub>16</sub> )						
1-nonene	(C <sub>9</sub> H <sub>18</sub> )						
1-decene	(C <sub>10</sub> H <sub>20</sub> )						
1-undecene	(C <sub>11</sub> H <sub>22</sub> )						
1-dodecene	(C <sub>12</sub> H <sub>24</sub> )						
1-tridecene	(C <sub>13</sub> H <sub>26</sub> )						
1-tetradecene	(C <sub>14</sub> H <sub>28</sub> )						
1-pentadecene	(C <sub>15</sub> H <sub>30</sub> )						
<b>Cyclic hydrocarbons</b>		<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>
Cyclopentene	(C <sub>5</sub> H <sub>8</sub> )						
Cyclopentane	(C <sub>5</sub> H <sub>10</sub> )						
Cyclohexene	(C <sub>6</sub> H <sub>10</sub> )						
Cyclohexane	(C <sub>6</sub> H <sub>12</sub> )						
Cycloheptene	(C <sub>7</sub> H <sub>12</sub> )						
Cycloheptane	(C <sub>7</sub> H <sub>14</sub> )						
<b>Aromatics</b>		<b>22.3493</b>	<b>20.8560</b>	<b>19.6935</b>	<b>19.2202</b>	<b>19.0992</b>	<b>19.0949</b>
Benzene	(C <sub>6</sub> H <sub>6</sub> )	19.3317	18.6104	17.9544	17.7893	17.8756	18.0266
Toluene	(C <sub>7</sub> H <sub>8</sub> )	2.8490	2.1436	1.6729	1.3839	1.1883	1.0408
Ethylbenzene	(C <sub>8</sub> H <sub>10</sub> )	0.0105	0.0075	0.0057	0.0046	0.0038	0.0033
O-xylene	(C <sub>8</sub> H <sub>10</sub> )	0.0381	0.0235	0.0155	0.0111	0.0084	0.0066
M-xylene	(C <sub>8</sub> H <sub>10</sub> )	0.0858	0.0507	0.0321	0.0222	0.0164	0.0125
P-xylene	(C <sub>8</sub> H <sub>10</sub> )	0.0341	0.0203	0.0130	0.0090	0.0067	0.0051
<b>Short chains alcohols, ketone and carboxylic acids</b>		<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>	<b>0.0000</b>
Methanol	(CH <sub>4</sub> O)						
Ethanol	(C <sub>2</sub> H <sub>6</sub> O)						
Propanol	(C <sub>3</sub> H <sub>8</sub> O)						
Acetone	(C <sub>3</sub> H <sub>6</sub> O)						
Acetic acid	(C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )						
Acrylic acid	(C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> )						
<b>Total</b>		<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>

accounted for by H<sub>2</sub>, CO and CO<sub>2</sub>. Traces of water and light olefins (ethylene and propylene) were also predicted. No solid carbon, alcohols, ketones and carboxylic acids were predicted. The data show that the increase in temperature decreases the CH<sub>4</sub>, aromatics and CO<sub>2</sub> formation at equilibrium. For example at 350°C compositions of ca. 62.8% for CH<sub>4</sub>, 22.35% for aromatics and 7.9% for CO<sub>2</sub> were predicted compared to ca. 56.9%, 19.1%, 0.052% for CH<sub>4</sub>, aromatics and CO<sub>2</sub> respectively at 600°C. On the other hand CO and H<sub>2</sub> have been predicted to increase with the increase in temperature. The aromatics can be condensed as liquid fuel and the remaining gas mixture can be used as combustible or can undergo subsequent transformation to, for example, produce syngas with H<sub>2</sub>/CO ratios of ca. 2/1 suitable for Fischer-Tropsch process to produce liquid fuel. Fig. 1 shows the selectivity of the carbon in the vegetable oil to CO, CO<sub>2</sub>, CH<sub>4</sub> and aromatics as a function of temperature. The selectivity to CH<sub>4</sub> almost remains constant throughout the entire selected temperature range while that of aromatics and CO<sub>2</sub> decreases with temperature and becomes temperature insensitive from 500°C and above. The carbon selectivity to CO increases with the temperature and also becomes temperature insensitive from 500°C and above. The predicted data suggest that temperature from 500°C and above must be used to avoid CO<sub>2</sub> formation. At these temperatures, the carbon selectivities to CH<sub>4</sub> and aromatics all combined account for 90%.

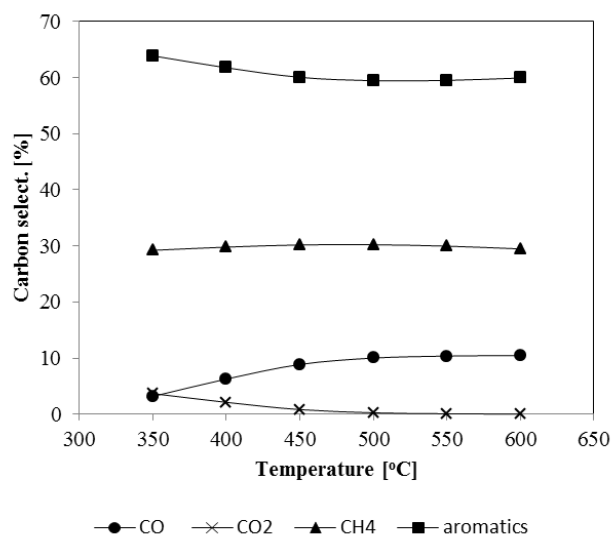


Fig. 1. Carbon selectivity to CO, CO<sub>2</sub>, CH<sub>4</sub> and aromatics

### B. Effect of feed dilution by inert

For an industrial application the vegetable oil cracking will require a catalyst that will be carried by an inert gas. For this reason, this section reports the effect of an inert gas on the vegetable oil cracking. N<sub>2</sub> was selected as inert and the effects of feed dilution on carbon selectivity to CO, CO<sub>2</sub>, CH<sub>4</sub> and aromatics are respectively presented in tables 2 to 5.

TABLE II  
 EFFECT OF FEED DILUTION ON CO SELECTIVITY (CARBON BASED %) AS FUNCTION OF TEMPERATURE

N <sub>2</sub> : Oil ratio	Temperature [°C]					
	350	400	450	500	550	600
1:1	3.23	5.79				
	9	6	8.617	9.934	10.345	10.465
10:1	3.66	6.91				
	9	0	9.242	10.149	10.410	10.486
100:1	5.99	8.96				
	7	4	10.127	10.422	10.495	10.515

TABLE III  
 EFFECT OF FEED DILUTION ON CO<sub>2</sub> SELECTIVITY (CARBON BASED %) AS FUNCTION OF TEMPERATURE

N <sub>2</sub> : Oil ratio	Temperature [°C]					
	350	400	450	500	550	600
1:1	3.642	2.363	0.953	0.294	0.090	0.030
10:1	3.427	1.807	0.641	0.187	0.057	0.019
100:1	2.264	0.780	0.199	0.052	0.015	0.005

TABLE IV  
 EFFECT OF FEED DILUTION ON CH<sub>4</sub> SELECTIVITY (CARBON BASED %) AS FUNCTION OF TEMPERATURE

N <sub>2</sub> : Oil ratio	Temperature [°C]					
	350	400	450	500	550	600
1:1	29.26	29.71	30.17	30.25	30.03	29.55
	5	6	4	6	0	4
10:1	29.38	29.96	30.29	30.25	29.94	29.37
	6	6	3	6	1	0
100:1	29.92	30.36	30.38	30.07	29.45	28.48
	4	9	4	0	6	8

TABLE IV  
 EFFECT OF FEED DILUTION ON AROMATICS SELECTIVITY (CARBON BASED %) AS FUNCTION OF TEMPERATURE

N <sub>2</sub> : Oil ratio	Temperature [°C]					
	350	400	450	500	550	600
1:1	63.85	62.12	60.25	59.50	59.51	59.91
	3	4	3	7	7	4
10:1	63.51	61.31	59.82	59.39	59.57	60.08
	7	6	1	8	2	6
100:1	61.81	59.88	59.28	59.44	60.01	60.94
	4	5	6	7	2	9

A slight increase in carbon selectivity to CO was predicted with the increase in feed dilution in the range of 350 and 450°C. No significant effect of dilution on the carbon selectivity to CO was noted at temperatures of 500°C and above (table 2). Feed dilution decreases the loss of carbon through CO<sub>2</sub> formation as indicated by the decreases in selectivity to CO<sub>2</sub> at higher dilutions (table 3). No significant effect of feed dilution was predicted for the carbon selectivity to CH<sub>4</sub> (table 4) and aromatics (table 5).

#### IV. CONCLUSION

Cracking of vegetable oil in the 350 – 600°C temperature range was predicted to mainly produce CH<sub>4</sub> and aromatics and small amounts of H<sub>2</sub>, CO and CO<sub>2</sub>. The increase in cracking temperature decreases the CH<sub>4</sub>, aromatics and CO<sub>2</sub> molar proportion in the equilibrium product. Feed dilution slightly increases the carbon selectivity to CO in the 350-450°C range, decreases the carbon selectivity to CO<sub>2</sub> and has no significant effect on the carbon selectivity to methane and aromatics.

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