Prediction of products yield at the thermal cracking of vegetable oil

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Abstract. According to previous studies on the pyrolysis of vegetable oils, it resulted that the thermal cracking process is prone to produce large yields of ethylene, propylene, hydrogen and methane, comparable with the gas proceeding from the steam cracking of naphtha, but at much lower process temperature, this ensuring important energy savings. The studies are performed on very different raw materials and different reaction conditions, that being why at this moment it is very difficult to predict the products yield. This paper uses an analytical semi-empirical model (ASEM) developed at the University of Florida, by applying it to a different raw material. The ASEM model fits very well to our experimental data, obtained at higher temperature but some parameters have to be adjusted. In the end we confirm a set of systemic parameters to be used for the prediction of main products yield proceeding from vegetable oil in an extended range of temperatures.

Keywords: waste vegetable oil, cracking, olefins, systematics, ASEM
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1. Introduction

Vegetable oils are renewable resources for fuels production and petrochemicals due to their chemical composition have some similarities with the crude oil, both containing long chains of hydrocarbon. Despite the good olefin yields [1,2,3], the pyrolysis of vegetable oil is still not an industrial option, the main reason for this being the desire to preserve the food resources. However, there are opportunities such as non-food vegetable oils in large quantities (Copaiba, Jatropha oil, Jojobe oil) and waste cooking oil.

Experimental studies were carried out with canola [1,2], soybean [3], palm [1] sunflower oils [4], and also with fractions of C4-C18 saturated triglycerols and C18 unsaturated tryglycerols [1]. All demonstrated that the yields of olefins, aromatics and other valuable compounds are similar to that obtained in petroleum fractions steam cracking.

For the industrial scaling up, it is compulsory to know with accuracy the products yield. Every experimental study contained correlations of product yields with the temperature and raw origin. A very useful analytical semi-empirical method (ASEM) was developed at the University of Florida [2] in order to predict product yields.

In this work, we compare experimental results obtained at the thermal cracking of different oils [1, 4] with those predicted with the ASEM method [2], in order to conclude if the method can be applied with confidence.

2. The analytical semi-empirical model ASEM

The model was proposed by the Clean Combustion Technology Laboratory (CCTL) in Atlanta [2], after processing experimental data obtained in their laboratory [5-8].

It consists in three equations (Eq.1-3) for the prediction of products yields:

$$y(t) = w[L(T:T_0, D)]^p [F(T:T_0, D)]^q \quad (1)$$

where:

$$L(T:T_o, D) = \frac{\exp[(T-T_0)]}{1 + \exp[(T-T_o)/D]} \quad (2)$$

and:

$$F(T:T_0,D) = 1 - L(T:T_0)/D \qquad (3)$$

The significance of the symbols in Eqs (1-3) is listed below:

D- parameter of logistic (Eq.1)

F(T)-forgetting function (Eq.3)

L(T)-   learning   function   (Eq.2)

p,q- constants (Eq.1)

t- residence time

T- cracking temperature [K]

T_0- critical cracking temperature [K]

w- parameter of logistic function(Eq.1)

y_i= individual yield (% wt)

Y= total yield (% wt)

The five parameters involved in equations 1-3 are T_0, D, w, p and q. For the canola oil thermocracking, T_0= 648 K and D=313 K and w, p and q are specific for each individual product, as seen in **Table 1**[2]:

Table 1. Parameters of ASEM equations for canola oil thermocracking [2]

Olefins				
Parameter	C_2H_4	C_3H_6	i-C_4'	1-C_4'
w	25.0	15.5	1.2	0.8
p	1.0	1.0	0.9	1.5
q	0	0.03	0.04	0.04
Paraffins				
Parameter	CH_4	C_2H_6	C_3H_8	C_4H_{10}
w	11.6	8	1.33	8.1
p	1.0	0.8	0.6	0.9
q	0.01	0.02	0.03	0.04
Oxygenates				
Parameter	CH_4O (methanol)			
w	3.7			
p	0.3			
q	0.7			
Others				
Parameter	H_2	CO	CO_2	Coke
w	1.3	3	1.5	4.2
p	1.4	2	0.2	2
q	-0.1	-0.1	0.2	-0.1

2. Experimental data

We used our experimental data obtained at the steam cracking of waste frying vegetable oil in a micropilot plant, at atmospheric pressure, 650°C and steam-to-feed ratio 1:1 wt. The yields of different compounds were determined by material balance combined with composition of pyrolysis gas determined by up-to–date chromatographic analysis method Refinery Gas Analysis developed by Wasson on Agilent 6890 N with multiple columns and different detectors. The experiment is described in [4].

These data are presented in **Table 2** and were compared with data in literature obtained in other thermocracking experiments, at atmospheric pressure in presence of an inert gas (nitrogen or steam).

Table 2. Comparative experimental data for yields (% wt) of products in pyrolysis gas obtained at the thermal cracking of vegetable oils

Chemical compound	Yield, % wt in this experiment	Yield, % wt in Zamostny *et al.* [1] experiment	Yield, % wt in Sadrameli &Green [2] experiment
CH_4	11.2	Data not found	10.6
C_2H_6	5.7	Data not found	7.0
C_2H_4	19.8	28.0	23.7
C_3H_8	0.8	Data not found	1.15
C_3H_6	6.1	10.5	13.6
H_2	4.4	Data not found	1.66
CO_2	4.3	15.8	3.87
i-C_4H_8	0.1	Data not found	1
Linear C_4H_8	1.5	Data not found	2.0
C_4H_{10}	1.9	Data not found	6.67

Experimental data presented in Table 2 were obtained in similar experiments: continuous processes of thermal cracking, with inert gas carrier,

to prevent carbonaceous deposits. All refers to generic "vegetable oils" since products yields were comparable between different vegetable oils and even between vegetables oils and fossil gas oil [2].

These experimental data were obtained in very different temperature conditions: 650 ^{o}C in our experiment [4], 820°C in [1] and 500°C in [2]. Also, the carrier gas was different: steam in our experiment and nitrogen in [1,2].

3. Results and discussions

In **Table 2**, one can see similarities and differences:
-C_4 hydrocarbon yields in pyrolysis gas are similar but this is not relevant since it depends not only on the pyrolysis process but also on the cooling agent temperature determining how much C_4 remains in the liquid phase and how much is recovered in gas;
-CH_4 yield shows a clear tendency to increase with the temperature rise;
- C_2H_4 yield increases with temperature rise
- C_3H_6 and C_3H_8 yields should also increase with temperature rise but results are not conclusive.

Next step was the processing of our experimental data with the semiempirical model ASEM, using the parameters recommended in [2]. Results are shown in **Table 3**:

Using the ASEM model, some of data fitted to its parameters: ethane, ethylene, hydrogen, propane and C_4 unsaturated hydrocarbons yields. For others, like methane, propylene, CO_2 and butane yields, the errors are important. For these, adjustment of parameters in Equations 1-3 should be done.

Table 3. Results of applying the parameters of ASEM model to experimental data

Chemical compound	Experimental yields, % wt	Calculated yields with ASEM model
CH_4	11.2	8.1
C_2H_6	5.7	5.9
C_2H_4	19.8	18.5
C_3H_8	0.8	1.0
C_3H_6	6.1	10.6
H_2	4.4	4.3
CO_2	4.3	1.1
i-C_4H_8	0.1	0.1
Linear C_4H_8	1.5	1.7
C_4H_{10}	1.9	5.6

Changing only the parameter w in equation 1, one can obtain better results for methane, propylene, and CO_2 yields. For methane, new w=16.04 instead of 11.6, for propylene let's keep w= 15.5, for CO_2: w=4.9 instead of 1.5. For butane, it is no point to adjust the parameters, since it is shared between the liquid and the vapour phase and the share depends on the cooling agent temperature.

In order to validate these new values for w, they will be applied together with the other parameters p and q (see **Table 1**) in Equations 1-3, in order to calculate the yields of these three components and to compare them with the experimental data at 400°C, 450°C, 500°C presented in [2]. Also, we present comparatively our experimental results with those calculated with new parameters, in the **Table 4**.

Table 4. Comparison of experimental yields in [2] and [4] with those calculated with adjusted w parameter in Eq.1

Product	Yield, % wt Ref [2] (t=400^{0}C)			Yield, % wt Ref [2] (t=450°C)			Yield, % wt Ref [2] (t=500°C)			Yield, % wt Ref [4] (t=650°C)		
	Exp.	Calc.	Error %	Exp.	Calc.	Error %	Exp.	Calc.	Error %	Exp.	Calc.	Error %
CH_4	7.1	8.28	-16.6	9.95	8.91	+10.5	10.6	9.54	+10.0	11.2	11.3	-1.3
C_3H_6	10.3	7.7	+25.2	12.25	8.5	+30.6	13.6	9.1	+33.1	6.1	10.6	-73.8
CO_2	2.9	3.7	-27.6	3.75	3.70	+1.3	3.87	3.8	+1.8	4.3	3.6	+16.3

As seen in Table 4, an adjustment of parameter *w* for CH_4 and for CO_2 can be made with satisfactory results at least in the range of $450^{\circ}C$-$650^{\circ}C$. As for C_3H_6 the results are unsatisfactory even for the parameters applied on the experimental data being the source of the ASEM model. The parameters can be adjusted as follows:

-   w=15.5
-   p=0.5
-   q=0.03   (4)

This will fit very well to the data in the original study [2] with relative errors between 4.9-5.7%, but our results at $650^{\circ}C$ are far from being described with accuracy by this model, and this is the same at $820^{\circ}C$[1]. This can be explained by consecutive reactions suffered by the propylene in the reactor at $650^{\circ}C$ in presence of water, most probably the decomposition.

4. Conclusions

The analytical semi-empirical model (ASEM) for the prediction of products yield at the thermal cracking of vegetable oil was originally worked out for canola oil in the temperature range 300-$500^{\circ}C$. This range can be extended to $650^{\circ}C$ for vegetable oil in general, with confidence, except for propylene yield. The model's parameters need small adjustments for methane and carbon dioxide.

In general, the original parameters of the ASEM method can be preserved with small adjustment for methane and carbon dioxide. A different set of systemic parameters for propylene yield prediction can be applied in a narrow range (400-$500^{\circ}C$) which is the usual temperature range.

This model can be improved by processing other experimental data when available.

5. References

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