**SUPLEMENTARY DATA**

**OF**

**Transient predictive model for dynamic analysis, kinetic study and reactor design of triglycerides transesterification to biodiesel**

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**A. Feed oil description.**

Triglycerides can be classified in two groups: simple triglycerides and mixed triglycerides. The simple triglycerides are composed by three identical fatty acid (*FA*) chains; however, these *FA* chains are not identical in a mixed triglyceride. Once the *pseudo-molecule* is built according with Fig. A.1, its thermodynamic properties can be estimated as explained in the Section 3 of the paper.

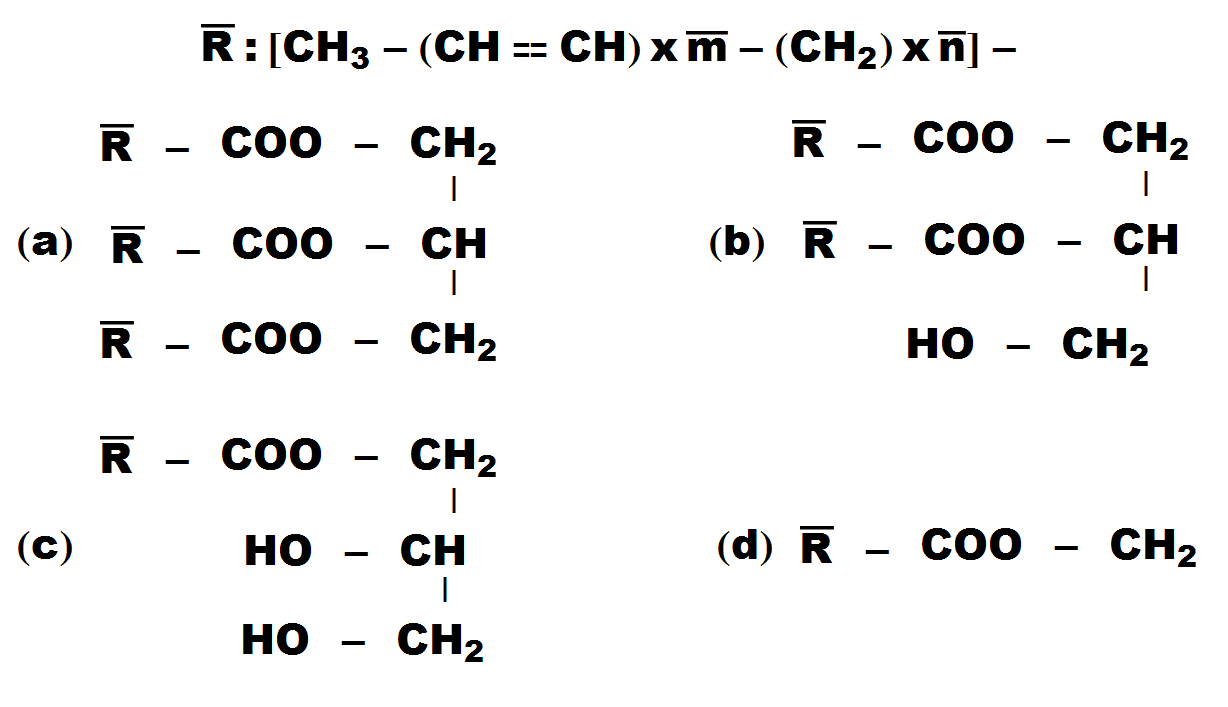


Figure A.1. Pseudo-molecule’s structures: a) triglyceride, b) diglyceride, c) monoglyceride and d) biodiesel.

In commercial processes the raw materials implemented in the transesterification process, in order to produce biodiesel, are conformed by mixtures of several oils and fats; therefore, the feed oil will be a complex blend of free fatty acids, simple triglycerides, which are composed of three identical fatty acid chains, and mixed triglycerides (fatty acid chains are not the same); besides, the fatty acid profile varies with each oil source implemented (Hoekman et al. 2012, 145-48) (Moser and Vaughn 2012, 34-36). It is well supported in the fact that the fatty acid composition of biodiesel fuels is essentially identical to their corresponding vegetable oil (Knothe 2008, 1358-59) (Knothe 2010, 364-70).

Many methods are unsuitable for estimating triglycerides thermophysics properties due to their complex structures and high molecular weights. The development of predictive models based on the molecular structure is important for an integral knowledge about the synthesis of the biodiesel fuel as well as to envisage or elucidate the fuel quality that will be obtained and how the properties change varying the different parameters of the model (Lopes et al. 2008, 749-50) (An et al. 2013, 647-49). For this reason, this section shows the implementation of some molecular group-contribution methods that have been widely employed to estimate numerical values of the properties of pure components, which are determined by the architecture of the molecules.

**B. Heat of formation of triglycerides.**

Table B.1 shows the groups, formation heats, and the molecules number of two different triglycerides: Linoleine and Euricine. Linoleine is the main triglyceride in *sunflower* and *soybean* oils, and Euricine is the main triglyceride in *brassica* *carinata* oil using a consistent set of molecular groups proposed in 2007 by Joback and Reid (Joback and Reid 2007, 233).

Table B.1. Groups and heat of formation values for Linoleine and Euricine. (R) denotes *Ring*.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Gk* | ∆*Hf*0 | *Nk*: LINOLEINE | | | | *Nk*: EURICINE | | | |
| TG | DG | MG | ME | TG | DG | MG | ME |
| CH3- | -76.45 | 3 | 2 | 1 | 2 | 3 | 2 | 1 | 2 |
| -CH2- | -20.64 | 36 | 24 | 12 | 12 | 54 | 36 | 18 | 18 |
| -CH= | 37.97 | 12 | 8 | 4 | 4 | 6 | 4 | 2 | 2 |
| -COO | -337.92 | 3 | 2 | 1 | 1 | 3 | 2 | 1 | 1 |
| (R)-CH2- | -26.80 | 2 | 2 | 2 | 0 | 2 | 2 | 2 | 0 |
| >CH- | 8.67 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 0 |
| OH- | -208.04 | 0 | 1 | 2 | 0 | 0 | 1 | 2 | 0 |

**C. Heat capability of fatty compounds.**

The set of functional groups (*CH3*, *CH*2, *COOH*, *CH*=*CH*, *COO*, *OH* and *CH*2-*CH*-*CH*2) shown in Table C.1 can represent all the molecular structures of the compounds present in the system, which are triglycerides (*TG*), diglycerides (*DG*), monoglycerides (*MG*), methyl esters (*ME*) and Glycerol (*GL*). The advantage of this methodology is in the use of *CH*2-*CH*-*CH*2 group, which is suitable to describe the glycerol fragment present in the acylglycerol molecules.

Table C.1 Number of k groups in the molecules that conforms the transesterification from Euricine and Linoleine to biodiesel used to calculate the heat capability.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Gk*: | *Nk*: LINOLEINE | | | | *Nk*: EURICINE | | | |
| TG | DG | MG | ME | TG | DG | MG | ME |
| *CH*3 | 3 | 2 | 1 | 2 | 3 | 2 | 1 | 2 |
| *CH*2 | 42 | 24 | 12 | 12 | 54 | 36 | 18 | 18 |
| *COOH* | 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| *CH*=*CH* | 6 | 4 | 2 | 2 | 3 | 2 | 1 | 1 |
| *OH* | 0 | 1 | 2 | 0 | 0 | 1 | 2 | 0 |
| *COO* | 3 | 2 | 1 | 1 | 3 | 2 | 1 | 1 |
| *CH*2-*CH*-*CH*2 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 0 |

**D. Thermal conductivity of fatty compounds.**

Table D.1 shows the set of bonds necessaries for full representing the molecules in the biodiesel synthesis, as well as its respective bond value. In order to illustrate the methodology, Table D.1 describes the number of bonds, which compose the fatty compounds present in the trilinoleine transesterification. *N* is the number of *C* atoms attached to group and it is considered as *N*= 17.

Table D.1. Bond group contribution and bonds number for the molecules that conforms the transesterification from Linoleine to biodiesel used to calculate the thermal conductivity.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Bond | Bond value | Number of bonds | | | | |
| TG | DG | MG | FAMEs | GL |
| C-H | 1162 | 98 | 67 | 36 | 34 | 5 |
| C-C | -2176 | 44 | 30 | 16 | 14 | 2 |
| (C=O)-OC | (-124×N)-393\* | 3 | 2 | 1 | 1 | 0 |
| (C-OH)’ | 4235 | 0 | 1 | 2 | 0 | 3 |
| C-OH | (-1826×N)+7642 | 0 | 0 | 0 | 0 | 0 |
| C=C | 136 | 6 | 4 | 2 | 2 | 0 |

**E. Density of fatty compounds.**

Table E.1 describes the type and number of groups which compose the fatty compounds present in the *trilinoleine* transesterification according to this methodology.

Table E.1. Extended group contribution *GCVOL* parameters used to calculate the liquid density.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Group* | *TG* | *DG* | *MG* | *FAME* | *G* | *Ak* | *Bk(1×103)* | *Ck(1×105)* |
| -CH3 | 3 | 2 | 1 | 2 | 0 | 16.43 | 55.62 | 0 |
| -CH2- | 35 | 23 | 12 | 11 | 0 | 12.04 | 14.1 | 0 |
| -CH= | 12 | 8 | 4 | 4 | 0 | -1.651 | 93.42 | -14.39 |
| -CH2COO- | 3 | 2 | 1 | 1 | 0 | 36.32 | -36.46 | 11.52 |
| >CH- | 1 | 1 | 0 | 0 | 1 | 7.299 | -26.06 | 0 |
| -CH2OH | 0 | 1 | 2 | 0 | 3 | 36.73 | -71.25 | 14.1 |

**F. Viscosity of fatty compounds.**

Viscosity of fatty compounds is essential for the process design, simulation, and optimization because this property affects the flow characteristics, it also causes a loss of energy due to friction, and therefore, mass and heat transfer coefficients are affected as well. Table F.1 shows the functional groups that represent the molecular structures of fatty compounds that exist in the trilinoleine transesterification with methanol (*Ncs*=1), in order to compute the dynamic viscosity by mean of the aforementioned method.

Table F.1. Number of *k* groups in the molecules that conforms the methanolysis from Linoleine to biodiesel used to calculate the liquid viscosity. \* For methanolysis, *Ncs*= 1.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *Ncs*=1\* | *Nk* | | | | | | |  |  |
| Compound | CH3 | CH2 | COOH | CH= | OH | COO | CH2-CH-CH2 | Mwi | Nc |
| TG | 3 | 36 | 0 | 12 | 0 | 3 | 1 | 872 | 57 |
| DG | 2 | 24 | 0 | 8 | 1 | 2 | 1 | 612 | 39 |
| MG | 1 | 12 | 0 | 4 | 2 | 1 | 1 | 352 | 21 |
| FAME | 2 | 12 | 0 | 4 | 0 | 1 | 0 | 292 | 19 |
| G | 0 | 0 | 0 | 0 | 3 | 0 | 1 | 92 | 3 |
| MeOH | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 32 | 1 |