CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216 DOI: 10.3303/CET1545319

Experimental Study of Short Chain Oils Viscosity as Biodiesel Additives

Alexandra E. Bonet-Ruiz*[a], Valentin Pleşu[a], Jordi Bonet-Ruiz[b], Mădălina-Cosmina Tohăneanu[a], Joan Llorens[b], Marion Lepinay[c], Cecile Dineiro[c]

[a]University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, Bldg A, Room A056, RO-011061 Bucharest, Romania
[b]University of Barcelona, Department of Chemical Engineering, 1, Martí i Franquès Street, 6th Floor, E-08028 Barcelona, Spain
[c]IUT Lyon 1, Site de Villeurbanne Doua, Département Génie Chimique - Génie des procédés, 2-4, rue de l'Emetteur, 69622 Villeurbanne cedex, France
a_bonet@chim.upb.ro

An increasing use of chemicals from biomass instead of non-renewable petrol-based ones is expected. For instance, the anaerobic digestion of organic residual streams generates many useful chemicals for the industry, together with short chain fatty acids. Another example is the biodiesel who is a suitable substitute for the non-sustainable petro-diesel. The diesel industry is mature and the biodiesel one is still under development. Oils are too viscous to be used directly in the nowadays diesel engines, producing a bad combustion. A way to reduce the viscosity of oils is to convert them into biodiesel. Biodiesel production by transesterification of non-edible oils with alcohols generates glycerol as by-product and many nowadays studies focus on providing uses to it. There are many applications for glycerol but not enough for a high biodiesel production. A way to avoid the glycerol excess is to use it in the biodiesel formulation. For instance, glycerol reacts with short chain organic acids producing short chain oils that are useful biodiesel additives. The present study determines and correlates the viscosity of short chain fatty acids (triacetin, tripropionin and tributyrin) and compares it to the viscosity of methyl oleate and solketal (another feasible biodiesel additive). The results show that short chain oils present a low enough viscosity to be used in biodiesel formulation. The viscosity model obtained is used to evaluate the viscosity of the biodiesel that would result, considering several literature experiments related to acid-genesis stages using different residual streams. The results show that the short chain fatty acids mixture obtained from any anaerobic digestion is useful as biodiesel additive. Although the short chain oil triacetin is technically a good biodiesel additive, it cannot be used in European Union due to biodiesel legal limitations on the maximum amount of triglycerides; these limitations are not present in the equivalent USA regulations.

1. Introduction

Glycerol is a by-product of biodiesel synthesis by transesterification and its market is saturated. A solution is to convert it into a biodiesel additive. Glycerol is biodegradable and can be used as substrate in biochemical processes to produce acids and alcohols, e.g. 1,3-propanediol, citric acid, succinic acid, or oils (Duarte and Maugeri, 2014). However, these compounds and hydrogen, methane or short chain fatty acids can be also obtained from lower quality wastewater organic streams, e.g. oil from brewery wastewater (Mata et al, 2014). Glycerol is preferable to be used directly as it is, as raw material, rather than in processes where it is partially degraded. Several short chain oils have been proved to be good biodiesel additives, e.g. triacetine (Casas et al, 2010) or 5 % tripropionin (Herseczki et al., 2013). Rahuet et al. (2013) pointed out that other short chain oils such as tripropionin, tributyrin or tributyrate can be also good biodiesel additives for lubricity and viscosity improvement. Biodiesel quality depends on its formulation (Bokhari et al., 2014). Short chain oils can be obtained reacting glycerol with short chain fatty

Please cite this article as: Bonet-Ruiz A., Pleşu V., Bonet-Ruiz J., Tohăneanu M.C., Llorens J., Lepinay M., Dineiro C., 2015, Experimental study of short chain oils viscosity as biodiesel additives, Chemical Engineering Transactions, 45, 1909-1914 DOI:10.3303/CET1545319

acids. The reaction of organic acids with glycerol can be catalysed by supported sulfonic acids (Ladero et al., 2009) or even without catalyst (Galan et al., 2009). Most organic waste streams provide short chain fatty acids by anaerobic digestion in the first acids generation step, e.g. acetic, propionic, n-butyric, iso-butyric, caproic acid. Volatile fatty acids are also obtained as by-products of many alcohols and acids using biotechnology. These acids can be separated from the aqueous media using an anion exchange resin, even in the presence of other compounds, e.g. ethanol (Lu et al., 2012). Regeneration can be produced with glycerol, obtaining short chain fatty acids oils suitable as biodiesel additives. The ion exchange resin can act as adsorbent and catalyst to retain all kind of free fatty acids from vegetable oil and to convert them to biodiesel (Shibasaki-Kitakawa et al., 2013). The proportion between the collected short chain acids depends on retention time, substrate concentration, type of microorganisms, temperature, and pH. Their proportion once converted to short chain oil and blended with biodiesel influences the biodiesel properties. Biodiesel viscosity at low temperature depends on the vegetable oil used as raw material, additives used and blending. The scope of the present study is to determine experimentally the viscosity of these compounds and mixtures and their influence on biodiesel viscosity. Several examples in literature where short chain fatty acids are produced as by-product are presented and their suitability as raw material for biodiesel additive synthesis is evaluated. The effect of pH and short chain acids distribution on the final biodiesel obtained is evaluated using AspenPlus® properties estimation tool.

2. Material and method

The most advantageous short chain oils pointed out by Rahuet et al. (2013) have been used: triacetin, tripopionin and tributyrin. Methyl oleate is used as a representative compound of biodiesel. Solketal is a biodiesel additive derived also from glycerol. Although all the chemical compounds used are purchased from Sigma-Aldrich, some of them are produced by some other companies. Triacetin with 99 % purity is manufactured by Eastman Chemical Company and distributed by Aldrich with reference number 525073-1 L. Tripropionin, Kosher reference W328618-1kg-K with 99 % purity and tributyrin reference W222305-1kg with 97 % purity are produced by SAFC. A sample of 100 mL a purity of tributyrin higher than 99 % with reference T8626-100 mL from Sigma Aldrich is also used. The methyl oleate is of technical grade 70 % from Sigma Aldrich with reference 268038-1L. The solketal (DL-1,2-Isopropylideneglycerol) reference 122696-100g has 98 % purity and was purchased from Sigma Aldrich.

The viscosity of the oils is determined using a conical spindle in a rotational rheometer HAAKE Mars Thermoscientic with the software HAAKE Rheowin Job Manager. The conical spindle of 60 mm diameter and 1° angle is found to be the most suitable, the gradient was fixed at 300 s^{-1}. Samples of less than 2 mL of oil are required to fill the capsule without covering the spindle. The sample temperature in the rheometer is controlled using a thermostated bath HAAKE C25 and its display HAAKE F6. The metallic capsule was properly insulated using polyester to avoid heat losses but without interfering with the free movement of the spindle and measurements. The measurements start when the temperature becomes stable and it is let to evolve until the rheometer measured signal becomes linear and stable for some time. At low temperatures, the temperature is first stabilized with the capsule empty to avoid contaminating the samples with condensed air moisture. The scale is adjusted for a better visualization of the results and the shear stress is adjusted to avoid oscillations. The measurements performed in 1 minute on the stabilized apparatus are averaged and used to calculate the viscosity of the sample. The viscosities at 298 K are also measured with a capillary viscosimeter Proton 3747/150. The viscosity of mixtures is determined according to Eq(1) to Eq(3) once the parameters are regressed. The data regression of pure compounds is performed using the modified Andrade equation - Eq(3). A third correction term is added to the equation of Andrade for a better fitting because the region of temperatures evaluated is quite large. The viscosity of binary mixtures is regressed according to Eq(1) and the interaction effect between compounds of the mixture is taken into account with the correction factors presented in Eq(2). The correction is required to take into account that in some cases the viscosity is not proportional to the composition and that methyl oleate mixtures at high temperatures have a lower viscosity than the corresponding pure compounds.

$$\ln \eta^{l} = \sum_{i} x_i \cdot \ln \eta_i^{*l} + \sum_{i} \sum_{j} \left(k_{ij} \cdot x_i \cdot x_j + m_{ij} \cdot x_i^2 \cdot x_j^2 \right) \quad (1)$$

where:

$$k_{ij} = a_{ij} + \frac{b_{ij}}{T} \text{ and } m_{ij} = c_{ij} + \frac{d_{ij}}{T} \quad (2)$$

$$\ln \eta_i^{*l} = A_i + \frac{B_i}{T} + C_i \cdot \ln T \quad (3)$$

η^l is the viscosity of the mixture, η_i^{*l} is the viscosity of the pure compound i, x_i is the mass fraction of compound i, T is the absolute temperature and the rest are constants.

3. Results

3.1 Experimental viscosity determination

A biodiesel additive must not increase substantially the biodiesel viscosity, therefore the viscosity of the proposed short chain oils as biodiesel additives is determined experimentally and compared to the viscosity of methyl oleate (a biodiesel compound) and to another biodiesel additive (solketal) see Figure 1. The viscosities obtained at 278 K using the capillar viscosimeter coincides with the viscosities determined with the rheometer. The viscosity of short chain oil binary mixtures is also determined and presented in Figure 2. Finally, the binary mixtures of short chain oils and methyl oleate are determined to evaluate their influence as biodiesel additives see Figure 3. Viscosity experimental data are correlated using multilineal regressions. The parameters of Eq(1) are presented in Table 1 and the parameters of Eq(2) in Table 2.

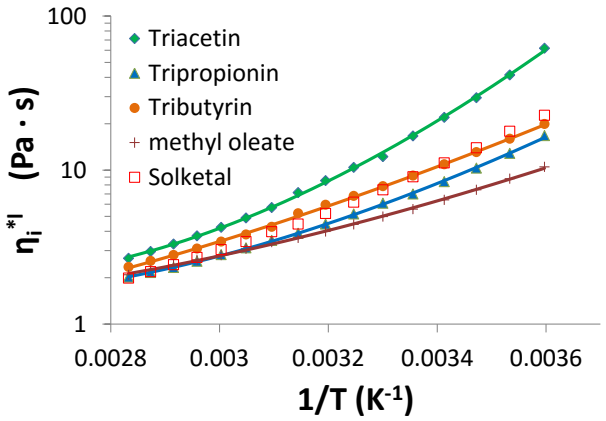

Figure 1: Pure compounds viscosities and correlation

Table 1: Andrade constants for pure compounds viscosities (viscosity in Pa.S). Confidence interval of 95 %

	Triacetin	Tripropionin	Tributyrin	Biodiesel	Solketal
A	-336.82±40	-197.58±21	-102.96±29	-110.37±24	-183.88±14
B	19,142±1875	11,543±962	7,237±1355	6,934±1101	11,303±628
C	48.342±6	28.226±3	14.199±4	15.594±4	26.005±2
r2	0.9993	0.9995	0.9992	0.9990	0.9998

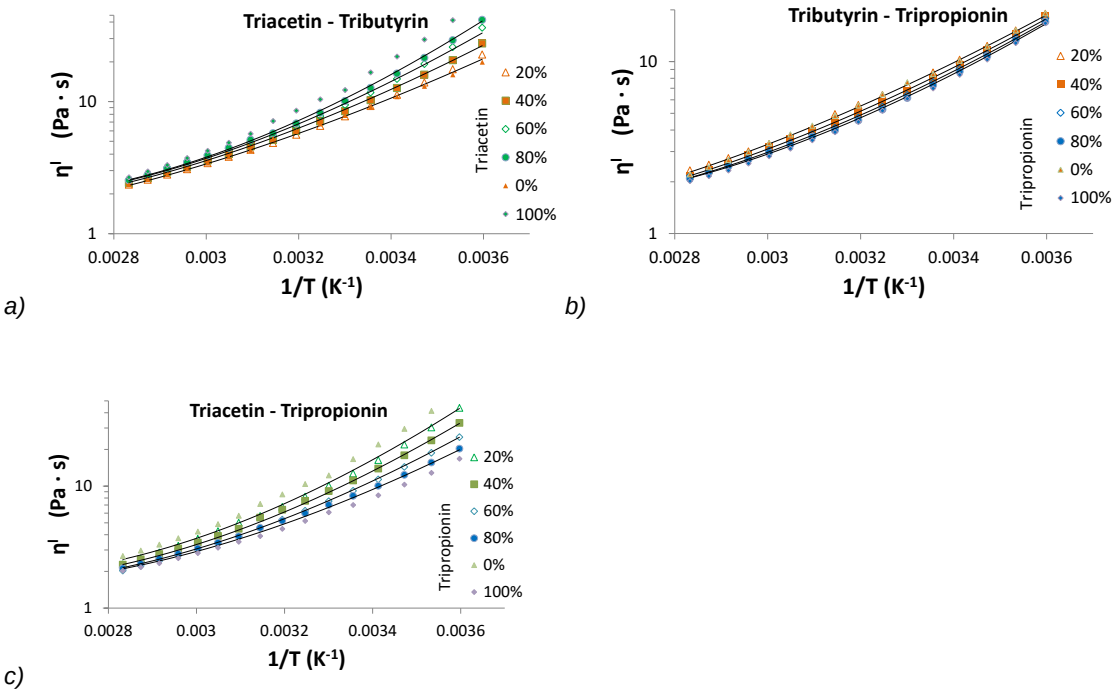

Figure 2: Short chain oil mixtures viscosities and correlation

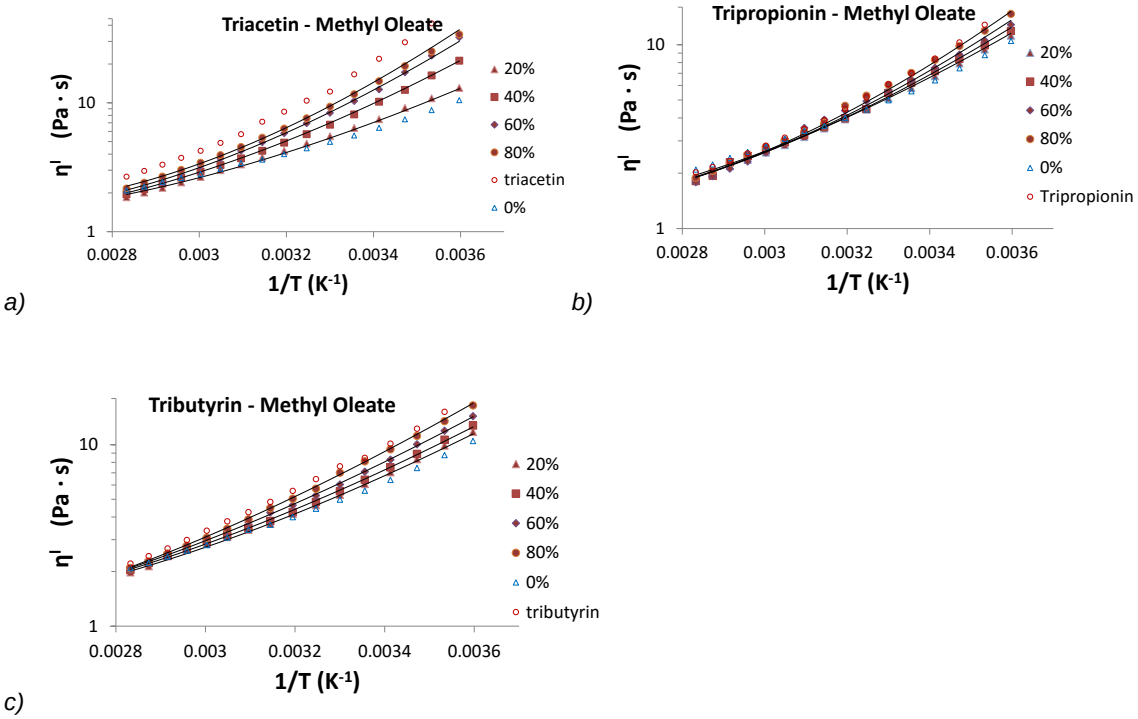

Figure 3: Short chain oils and methyl oleate mixtures viscosities and correlation at different mass percentages of short chain oils

Table 2: Andrade constants for binary interaction viscosities (viscosity in Pa.S) and coefficient of correlation of parameters regressed and between experimental and regressed viscosities

	Triacetin Tributyrin	Tripropionin Tributyrin	Triacetin Tripropionin	Triacetin Biodiesel	Tripropionin Biodiesel	Tributirin Biodiesel
a	2.1466±1.7	0.90575±0.8	1.6656±1.6	1.6110±1.3	-2.3496±0.82	-2.1734±0.5
b	-843.52±527	-269.82±252	-317.46±521	-795.03±409	711.10±258	145.13±145
c	-4.6593±7.8	-3.1995±3.7	-3.7762±7.6	-13.884±6.0	6.2038±3.8	8.36199±2.1
d	1,970.6±2,413	884.05±1,155	1,099.8±2,385	5,351.1±1,874	-1,958.1±1,181	-2,550.7±664
r2	0.8163	0.4244	0.6501	0.9160	0.5546	0.8510
r2 n	0.9987	0.9995	0.9993	0.9984	0.9986	0.9995

3.2 Evaluation of several short chain oil sources

The proportion of short chain fatty acids produced from residual streams acid-generation fermentation depends on the pH, concentration, temperature, kind of microorganism, type of substrate, residence time and the sort of operation. The short chain fatty acids are rarely the desired product and they are collected as an undesirable by-product. The study of Syngiridis et al. (2014) shows that a great production of a certain short chain fatty acid is attained choosing the suitable operation conditions, e.g. butyric acid from glucose (case A). Therefore, the residual streams used as examples of suitable sources of short chain fatty acids by Rahuet et al. (2013) are used as illustrative examples. A new study of Syngiridis et al. (2014) optimizing the amount of butyric acid is also considered. It is assumed that only the acetic, propionic and butyric acids are collected and used for glycerol valorisation and the other compounds, e.g. carboxylic acids and alcohols, are used for other purposes. The short chain oils mixture obtained is mixed with methyl oleate according to the molar ratio 1:3 corresponding to the fact that in the biodiesel synthesis 1 mol of glycerol is generated for each 3 mols of biodiesel. The additive-biodiesel composition from the several sources is presented in Table 3.

Table 3: Molar additive-biodiesel composition from several substrates

wastewater	Triacetin	Tripropionin	Tributirin	Biodiesel	% mass additive
Pre-treatment sludge	0.1303	0.0779	0.0418	0.7500	21.6
Activated sludge	0.1336	0.0765	0.0400	0.7500	21.6
Secondary sludge	0.1364	0.0753	0.0383	0.7500	21.5
Pig slurry	0.1215	0.0575	0.0710	0.7500	22.1
Cattle slurry I	0.1914	0.0337	0.0249	0.7500	20.7
Cattle slurry II	0.1912	0.0338	0.0250	0.7500	20.7
Olive mill	0.1655	0.0536	0.0309	0.7500	21.1
High strength molasses	0.1291	0.1032	0.0177	0.7500	21.4
Glucose	0.1200	0.0201	0.1099	0.7500	22.5
Glucose (case A)	0.0146	0.0102	0.2252	0.7500	25.0

Table 4 shows the viscosities at different temperatures of the resulting biodiesel from the compounds shown in Table 3. The kinematic viscosity of biodiesel at 313 K must be between 3.5 and 5 mm^2/s that correspond to a dynamic viscosity between around 4 and 9 Pa s. Therefore, although tripropionin is the compound with a lower viscosity, all the evaluated mixtures avoid the problems associated to poor combustion due to high viscosities during the diesel injection. Therefore, it can be concluded that short chain oils collected from any source are usable as biodiesel compounds.

4. Conclusions

The viscosity of short chain oils mixtures has been experimentally determined and regressed. Tripropionin is the short chain oil with lowest viscosity. The obtained model is used to evaluate the viscosity of biodiesel mixtures with different proportions of short chain fatty acids depending on its source. All the mixtures evaluated have suitable viscosities when mixed with biodiesel. The lowest viscosity is obtained for a mixture of tributyrin and methyl oleate (or biodiesel). The highest viscosities are obtained for triacetin. The proportion of short chain oils and therefore the viscosity of the obtained oil can be regulated according to the pH of the acidogenesis step. For instance, a viscosity of 4 Pa.S at 313 K is obtained with a binary

mixture of triacetin and propionin with 85 % wt of triacetin once mixed with 79.9 % wt methyl oleate. Hence, legal limitations on the maximum amount of triglycerides should be revised.

Table 4: Calculated viscosity of additive-biodiesel mixtures at several temperatures

Wastewater	279 K	298 K	313 K	353 K
Pre-treatment sludge	9.96	5.23	3.51	1.73
Activated sludge	10.02	5.26	3.53	1.74
Secondary sludge	10.08	5.29	3.55	1.75
Pig slurry	9.12	4.84	3.26	1.62
Cattle slurry I	10.74	5.55	3.69	1.81
Cattle slurry II	10.73	5.55	3.69	1.81
Olive mill	10.40	5.42	3.62	1.78
High strength molasses	10.70	5.59	3.74	1.84
Glucose	8.11	4.36	2.96	1.49
Glucose (case A)	6.22	3.49	2.43	1.25
Average	*10.02*	*5.24*	*3.51*	*1.73*
Pure methyl oleate	10.49	5.58	3.99	2.09
Pure Triacetin	61.77	16.65	8.54	2.67
Pure Tripropionin	16.74	6.99	4.46	2.02
Pure Tributyrin	19.93	9.2	5.95	2.35
Triacetin+biodiesel	12.28	6.18	4.06	1.94
Tripropionin+biodiesel	11.20	5.93	3.98	1.95
Tributyrin+biodiesel	5.91	3.35	2.34	1.21
BD100			4.93	2.58

References

Bokhari A., Yusup S., Kamil R.N.M., Junaid A., 2014, Blending study of palm oil methyl esters with rubber seed oil methyl esters to improve biodiesel properties, Chemical Engineering Transactions, 37, 571-576.

Casas A., Ruiz J.R., Ramos M.J., Pérez A., 2010, Effects of triacetin on biodiesel quality, Energy and Fuels, 24(8), 4481-4489.

Duarte S.H., Maugeri F., 2014, Prediction of quality properties for biodiesel production by oleaginous yeast cultivated in pure and raw glycerol, Chemical Engineering Transactions, 37, 463-468.

Galan M.I., Bonet J., Sire R., Reneaume J.M., Plesu A.E., 2009, From residual to useful oil: Revalorization of glycerol from the biodiesel synthesis, Bioresource Technology, 100, 3775–3778.

Herseczki Z., Marton G., Dallos A., 2013, Synthesis of tripropionin from crude glycerol the by-product of biodiesel production, Studia Universitatis Babes-Bolyai Chemia, 2, 7-22.

Ladero M., Molinero L., Sanchez F., García-Ochoa F., 2009, Synthesis of triglycerides from cinnamic acid and glycerol using supported sulphonic acids, Chemical Engineering Transactions,17, 175-180.

Lu H., Sun Y., Zhang M., Geng Z., Ren M.,2012, Removal of Acetic Acid from Fuel Ethanol Using Ion-Exchange Resin, Energy Fuels, 26, 7299−7307.

Mata T.M., Santos J., Mendes A.M. Caetano N.S., Martins A.A., 2014, Sustainability evaluation of biodiesel produced from microalgae chlamydomonas sp grown in brewery wastewater, Chemical Engineering Transactions, 37, 823-828.

Rahuet A.R., Pleşu V., Ruiz J.B., Bonet Ruiz A.E., Llacuna J.L., 2013, Glycerin revalorization using anaerobic digestion of organic waste, Chemical Engineering Transactions, 35, 1015-1020.

Shibasaki-Kitakawa N., Kanagawa K., Nakashima K., Yonemoto T., 2013, Simultaneous production of high quality biodiesel and glycerin from Jatropha oil using ion-exchange resins as catalysts and adsorbent, Bioresource Technology, 142, 732-736.

Syngiridis K., Bekatorou A., Kandylis P., Larroche C., Kanellaki M., Koutinas AA., 2014, Favouring butyrate production for a new generation biofuel by acidogenic glucose fermentation using cells immobilised on γ-alumina, Bioresource Technology, 161,118-123.