# ESTIMATION METHODS FOR THERMOPHYSICAL PROPERTIES OF CAMELINA SATIVA CRUDE OIL

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*Camelina is one of the most promising sources of renewable fuels. The crude oil obtained from this plant can be chemically treated and converted into bio-diesel or bio-kerosene. To study straight camelina oil combustion process is very important to know as many of its properties as possible. In this article, estimation methods of several thermophysical properties, such as: critical properties, density, thermal conductivity, and specific heat are presented. Where it was possible, the estimated values have been compared with experimental measurements, thus validating the used method.*

**Keywords**: camelina oil, estimation methods, thermophysical properties

## 1. Introduction

Camelina oil is a new, promising feedstock for second generation bio-fuels. The bio-kerosene obtained from camelina oil meets all the performance and safety requirements so that it can be used in aviation. Blends of classic aviation fuel / bio-kerosene obtained from camelina oil have been successfully tested on fighting planes and passenger planes [1]. According to European directives 2003/30/CE and 2009/28/CE, crude vegetable oils are also considered biofuels. In the specialized literature, there is scarce information regarding the combustion process of crude vegetable oils, in particular camelina oil. The possibility of using straight camelina oil as fuel for terrestrial applications has been taken in consideration because the process of obtaining the vegetable oil is cheaper and less time consuming then obtaining biofuels from vegetable oils.

To understand better the combustion process of the crude camelina oil, is very important to know as many of its properties as possible. In this paper, estimation methods for several thermophysical properties are presented and applied for the particular case of crude vegetable camelina oil. To validate the used methods, the estimated values have been compared with experimental

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measurements, where such data were available. A detailed presentation of the experimental procedure used for obtaining the experimental data which will be presented in this paper, can be found in reference [2].

## 2. Camelina oil molar weight estimation

The calculations presented in this article are based on the fatty acids camelina oil chemical composition, given in Table 1. The camelina oil fatty acids composition has been analyzed at the Dangerous substances, waste and residual water testing laboratory from the National Research and Development Institute for Chemistry and Petrochemistry.

*Table 1*

**Camelina oil fatty acids composition**

| | Fatty acid | Molar fraction | Molar weight MWi (g/mol) |
|---|---|---|---|
| 1 | Palmitic acid(C16) | 0.0747 | 256 |
| 2 | Stearic acid (C18) | 0.0127 | 284 |
| 3 | Oleic acid (C18:1) | 0.1687 | 340 |
| 4 | Linoleic acid (C18:2) | 0.2449 | 282 |
| 5 | Linolenic acid (C18:3) | 0.3407 | 280 |
| 6 | Eicosanoic acid (C20:1) | 0.1479 | 278 |
| 7 | Behenic acid (C22) | 0.0042 | 310 |
| 8 | Erucic acid (C22:1) | 0.0058 | 338 |

The fatty acids composition of the camelina oil cultivated in Romania, and presented in Table 1, is similar, but not the same as those reported for oils obtained from camelina seeds cultivated in Spain [3] and in Slovenia [4]. The differences in the composition may be due to different cultivation regions and different growing conditions.

These fatty acids are found in the camelina oil in the form of triglycerides. The mathematical methods presented in this article estimate the termophysical properties of these triglycerides. The camelina oil thermophysical properties are calculated starting from these values and considering that the molar fraction of these triglycerides is equal with the molar fraction of the fatty acid in their composition.

The camelina oil molar weight has been calculated using the following relation [5]:

$$MW_{oil} = 3\sum x_i MW_i + 38.0488 \tag{1}$$

where $x_i$ represents the molar fraction of the fatty acid *i* in the oil's composition, and $MW_i$ is the molar weight of the respective fatty acid. According to equation (1), in order to estimate the molar weight of camelina oil is necessary to calculate first the weight average molecular weight of all the fatty acids components of the compound, based on their individual molecular weights and mole fractions. This is multiplied by 3 to take into account the 3 identical fatty acid chains found in the fatty acid corresponding triglyceride. In addition, one also needs to take into account the glycerol part of the triglyceride, which is composed of 3 carbon atoms and 5 hydrogen atoms (-$CH_2$-CH-$CH_2$-), as well as the difference of 3 hydrogen atoms between the fatty acids and the fatty acid chains in the composition of the triglyceride. The sum of these contributions, calculated using equation (2) [5], leads to the obtaining of the second term on the right-hand side of equation (1):

$$3 \cdot MW_{Carbon} + 5 \cdot MW_{Hidrogen} - 3 \cdot MW_{Hidrogen} = 38.0488 \quad (2)$$

By applying equation (1) the molar weight of the camelina oil has been estimated to *886.88 g/mol*.

### 3. Critical properties estimation methods

To determine the thermophysical properties of a substance, estimation methods use as input data the characteristic constants of the respective compound, defined in the following: normal boiling point, critical temperature, critical pressure, critical volume and acentric factor. To determine experimentally these constants is very difficult, because the majority of substances chemically decompose before reaching the critical point.

The critical temperature represents the temperature value above which the substance can no longer be liquefied, no matter how much pressure is applied. The critical pressure is the pressure of the substance's vapor pressure at the critical temperature. The critical volume is the volume occupied by 1 mole of substance at its critical temperature and pressure. The normal boiling point represents the temperature value at which the compound's vapor pressure is equal to the atmospheric pressure [6]. The acentric factor is a measure of the sphericity of the molecule [7].

The used estimation methods are presented in Table 2.

*Table 2*

**Critical properties estimation methods**

| Method | Equation |
|---|---|
| Joback [7] | $T_b[K] = 198 + \sum x_i \cdot \Delta T_{bi}$ (3) |
| | $T_c[K] = T_b \left[ 0.584 + 0.965 \sum x_i \cdot \Delta T_{ci} - \left( \sum x_i \cdot \Delta T_{ci} \right)^2 \right]^{-1}$ (4) |
| | $P_c[bar] = \left( 0.113 + 0.0032 \cdot n_A - \sum x_i \Delta P_{ci} \right)^{-2}$ (5) |
| | $V_c[cm^3/mol] = 17.5 + \sum x_i \Delta V_{ci}$ (6) |
| Constantinou & Gani [8] | $T_b[K] = 204.359 \cdot \ln(\sum x_i \cdot \Delta T_{b1i} + \sum y_i \cdot \Delta T_{b2i})$ (7) |
| | $T_c[K] = 181.128 \cdot \ln(\sum x_i \cdot \Delta T_{c1i} + \sum x_i \cdot \Delta T_{c2i})$ (8) |

| | |
|---|---|
| | $P_c[bar] = (\sum x_i \cdot \Delta P_{c1i} + \sum y_i \cdot \Delta P_{c2i} + 0.10022)^{-2} + 1.3705$ (9) <br> $V_c[cm^3/mol] = -0.00435 + (\sum x_i \cdot \Delta V_{c1i} + \sum y_i \cdot \Delta V_{c2i})$ (10) |
| Fedor [6,9] | $T_c[K] = 535 \cdot \log_{10}(\sum x_i \cdot \Delta T_{ci})$ (11) <br> $V_c[cm^3/mol] = 26.6 + \sum x_i \cdot \Delta V_{ci}$ (12) |
| Marrero & Gani [10] | $T_b[K] = 222.543 \cdot \ln(\sum x_i \cdot \Delta T_{b1i} + \sum y_i \cdot \Delta T_{b2i})$ (13) <br> $T_c[K] = 231.239 \cdot \ln(\sum x_i \cdot \Delta T_{c1i} + \sum x_i \cdot \Delta T_{c2i})$ (14) <br> $P_c[bar] = (\sum x_i \cdot \Delta P_{c1i} + \sum y_i \cdot \Delta P_{c2i} + 0.108998)^{-2} + 5.9827$ (15) <br> $V_c[cm^3/mol] = 7.95 + (\sum x_i \cdot \Delta V_{c1i} + \sum y_i \cdot \Delta V_{c2i})$ (16) |
| Nannoolal [11] | $T_b[K] = \frac{\sum x_i \cdot \Delta T_{bi}}{n^{0.6583} + 1.6868} + 84.3395$ (17) |
| Banks [12] | $\log_{10} T_b[K] = 2.98 - 4/\sqrt{M}$ (18) |
| Burnop [12] | $\log_{10} T_b[K] = \sum x_i \cdot \Delta T_{bi} / M - 8/\sqrt{M}$ (19) |

The results obtained using the above estimation methods are summarized in Tables 3 - 6.

*Table 3*

**Estimation of normal boiling point $T_b$**

| *$T_b$[K]* | *Joback* | *Constantinou & Gani* | *Gani & Marrero* | *Nannoolal* | *Banks* | *Burnop* |
|---|---|---|---|---|---|---|
| Tripalmitin | 1,540.5 | 806.66 | 825.51 | 909.78 | 690.41 | 893.49 |
| Tristearin | 1,677.78 | 827.41 | 847.72 | 946.93 | 701.33 | 918.25 |
| Triolein | 1,690.26 | 827.39 | 849.66 | 1,030.36 | 700.59 | 921.81 |
| Trilinolein | 1,702.74 | 827.37 | 851.58 | 1,113.79 | 699.85 | 925.43 |
| Trilinolenin | 1,715.22 | 827.36 | 853.48 | 1,197.24 | 699.11 | 929.13 |
| Trieicosanoin | 1,815.06 | 846.25 | 867.91 | 981.59 | 710.28 | 750.07 |
| Tribehenin | 1,952.34 | 863.49 | 886.42 | 1,014.16 | 719.49 | 960.51 |
| Trierucin | 1,964.82 | 863.48 | 888.05 | 1,089.35 | 718.91 | 963.74 |
| **Camelina oil** | **1,710,95** | **828,65** | **852,33** | **1,090.23** | **700.49** | **897.66** |

*Table 4*

**Estimation of critical temperature**

| *$T_c$[K]* | *Joback* | *Constantinou & Gani* | *Gani & Marrero* | *Fedor* |
|---|---|---|---|---|
| Tripalmitin | 3,008.84 | 958.80 | 1,009.48 | 1,020.29 |
| Tristearin | 4,487.05 | 976.93 | 1,031.86 | 1,042.35 |
| Triolein | 4,019.29 | 977.88 | 1,035.11 | 1,043.28 |
| Trilinolein | 3,665.24 | 978.82 | 1,038.31 | 1,044.22 |
| Trilinolenin | 3,389.76 | 979.76 | 1,041.47 | 1,045.16 |
| Trieicosanoin | 8,638.16 | 993.41 | 1,052.26 | 1,062.49 |

| | | | | |
|---|---|---|---|---|
| Tribehenin | 94,741.78 | 1,008.51 | 1,071.01 | 1,081.03 |
| Trierucin | 23,514.85 | 1,009.31 | 1,073.75 | 1,081.82 |
| **Camelina oil** | **4,824.19** | **979.53** | **1,038.60** | **1,045.23** |

*Table 5*

**Estimation of critical pressure**

| *$P_c$[bar]* | *Joback* | *Constantinou & Gani* | *Gani & Marrero* |
|---|---|---|---|
| Tripalmitin | 2.72 | 3.66 | 7.51 |
| Tristearin | 2.27 | 3.28 | 7.24 |
| Triolein | 2.43 | 3.33 | 7.28 |
| Trilinolein | 2.61 | 3.39 | 7.32 |
| Trilinolenin | 2.82 | 3.44 | 7.36 |
| Trieicosanoin | 2.02 | 2.98 | 7.04 |
| Tribehenin | 1.65 | 2.75 | 6.88 |
| Trierucin | 1.84 | 2.78 | 6.91 |
| **Camelina oil** | **2.56** | **3.35** | **7.29** |

*Table 6*

**Estimation of critical volume**

| *$V_c$[cm$^3$/mol]* | *Joback* | *Constantinou & Gani* | *Gani & Marrero* | *Fedor* |
|---|---|---|---|---|
| Tripalmitin | 2,963.5 | 2,967.73 | 2,970.33 | 2,818.01 |
| Tristearin | 3,299.5 | 3,302.29 | 3,308.01 | 3,134.62 |
| Triolein | 3,239.5 | 3,253.96 | 3,265.62 | 3,094.68 |
| Trilinolein | 3,179.5 | 3,205.63 | 3,223.23 | 3,054.74 |
| Trilinolenin | 3,119.5 | 3,157.29 | 3,180.84 | 3,014.79 |
| Trieicosanoin | 3,635.5 | 3,636.84 | 3,645.69 | 3,381.14 |
| Tribehenin | 3,971.5 | 3,971.41 | 3,983.37 | 3,767.87 |
| Trierucin | 3,911.5 | 3,923.08 | 3,940.98 | 3,727.93 |
| **Camelina oil** | **3,228.31** | **3,250.64** | **3,266.67** | **3,085.15** |

There are no experimental data or information in the specialized literature regarding these properties for the camelina oil. In Table 7, values of the critical properties of similar vegetable oils and of triglycerides found in the composition of the camelina oil, available in the specialized literature, are presented.

*Table 7*

**Critical properties values found in the literature**

| *Substance* | *$T_b$ [K]* | *$T_c$ [K]* | *$P_c$ [bar]* | *$V_c$ [cm3/mol]* |
|---|---|---|---|---|
| Rapeseed oil | 584 [13] | 765 [13] | - | - |
| Jatropha oil | 623.6 [14] | 837.45 [14] | - | - |
| Tripalmitin | 689.87 [15]<br>675 [16] | - | - | - |
| Triolein | 692.10 [15] | 953 [17]<br>977 [18] | 3.602 [17]<br>3.34 [18] | 3090 [17]<br>3250 [18] |
| Tristearin | 682 [14] | - | - | - |

Comparing the literature data with the calculated data, it has been concluded that the best result for the normal boiling point has been obtained using the Banks method [12], while for the critical properties the best results have been obtained using the Constantinou & Gani method [8].

A method to verify the consistency of the critical properties values is to calculate the critic compressibility factor, given by the relation (20) [6]:

$$Z_c = \frac{P_c \cdot V_c}{R \cdot T_c} \tag{20}$$

This factor's value should be smaller than 0.291 [7]. In our case this factor has the value of 0.133.

Another important material constant which is used as input data in other estimation methods is the acentric factor. This factor is calculated using the relation (21) [7]:

$$Z_c = 0.291 - 0.08 \cdot \omega \tag{21}$$

For the camelina oil, the value of 1.96 has been obtained.

### 4. Density estimation methods

To estimate the density of camelina oil, two methods have been used: the Ihmels method [5] and the Zong method [5].

The calculation formula proposed by the Ihmels method is:

$$\rho = \frac{MW}{V} = \frac{MW}{\sum n_i \Delta v_i} \tag{22}$$

where $MW$ represents the molar weight and $V$ the molar volume. The molar volume is calculated by summing up the volume group contributions $\Delta v_i$ multiplied by the number of $i$ group's appearances in the compound, $n_i$. $\Delta v_i$ is calculated using the following temperature depending polynomial function [5]:

$$\Delta v_i = A_i + B_i T + C_i T^2 \tag{23}$$

The values of the structural group specific coefficients A, B and C are presented in reference [5].

The calculation formula proposed by the Zong method is [5]:

$$\rho = \frac{MW}{V} = \frac{MW}{\sum N_{frag,A} \cdot V_A(T)} \tag{24}$$

where $N_{frag.A}$ represents the number of fragment A present in the compound, and $V_A(T)$ represents the molar volume of the respective fragment. $V_A(T)$ is given by the following relation [5]:

$$V_A(T) = \frac{1 + B_{2,A} \cdot T}{B_{1,A}} \tag{25}$$

The values of coefficients $B_{1,A}$ and $B_{2,A}$ are presented in reference [5].

The results obtained by using the estimation methods presented above are summarized in Table 8.

*Table 8*

**Camelina oil density $\rho$ [kg/m$^3$]**

| *T[K]* | *Experimental data* | *Ihmels method* | *Error* | *Zong method* | *Error* |
|---|---|---|---|---|---|
| 261 | 943 | 968 | 2.62% | 946 | 0.27% |
| 263 | 940 | 966 | 2.74% | 944 | 0.43% |
| 265 | 937 | 964 | 2.86% | 942 | 0.60% |
| 271 | 933 | 958 | 2.69% | 938 | 0.57% |
| 276 | 931 | 953 | 2.41% | 934 | 0.41% |
| 284 | 926 | 946 | 2.19% | 929 | 0.34% |
| 288 | 924 | 943 | 2.03% | 926 | 0.26% |
| 289 | 923 | 942 | 2.05% | 925 | 0.29% |
| 290 | 922 | 941 | 2.07% | 925 | 0.33% |
| 294 | 921 | 938 | 1.81% | 922 | 0.14% |

Both methods have a good accuracy in estimating the camelina oil's density, as it can been observed from the data presented in Table 8. Comparing the two methods, the values obtained with the Zong method are in a very good agreement to the experimental data, having an error under 1%.

By extrapolating the obtained data on a larger temperature range than the one for which experimental data are available, it can be observed in Fig. 1 that the results obtained with the Zong method are very closed to the those obtained by extrapolating the experimental data, while the results obtained using the Ihmels method tend to diverge, starting from the temperature of 450 K.

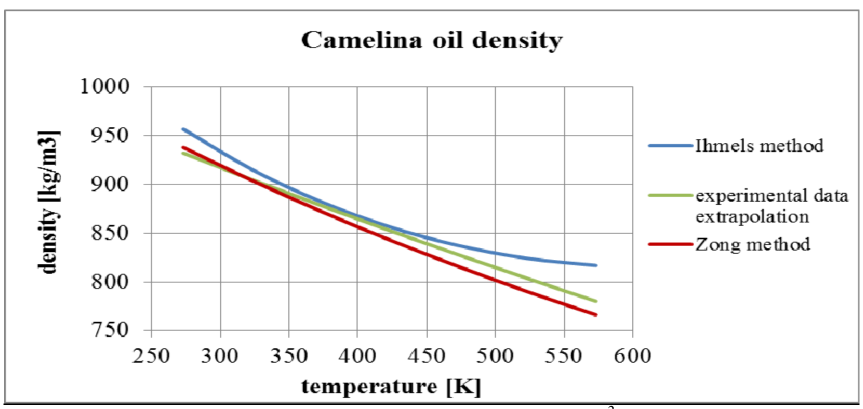


Fig. 1 Camelina oil density $\rho$ (kg/m$^3$)

## 5. Specific heat estimation methods

To estimate the camelina oil specific heat at constant pressure two methods have been used: the Ceriani method [5] and the Zong method [5].

The calculation formula proposed by the Ceriani method is:

$$C_p = \sum N_k \cdot (A_k + B_k \cdot T) \tag{26}$$

where $N_k$ represents the number of structural groups k present in the substance, and $A_k$ and $B_k$ are the method's coefficients specific to each structural group.

The values of parameters $A_k$ and $B_k$ used in the calculations are presented in [5].

The calculation formula proposed by the Zong method is:

$$C_p = \sum N_{frag.A} \cdot C_{p,A}(T) \tag{27}$$

where $N_{frag.A}$ represents the number of fragment A present in the substance, and $C_{p,A}(T)$ represents the specific heat of fragment A. $C_{p,A}(T)$ is calculated using the linear equation below:

$$C_{p,A}(T) = A_{1,A} + A_{2,A}(T) \tag{28}$$

The values of parameters $A_{1,A}$ and $A_{2,A}$, specific to each fragment, used in the calculations are presented in [5].

The results obtained by using the estimation methods presented above are summarized in Table 9.

*Table 9*

**Camelina oil specific heat $c_p$ [J/(kg·K)]**

| *T[K]* | *Experimental data* | *Ceriani method* | *Error* | *Zong method* | *Error* |
|---|---|---|---|---|---|
| 293 | 2,053 | 1,896 | 7.65% | 2,027 | 1.29% |
| 294 | 2,043 | 1,901 | 6.93% | 2,029 | 0.67% |
| 295 | 2,056 | 1,906 | 7.30% | 2,031 | 1.22% |
| 296 | 2,070 | 1,911 | 7.66% | 2,033 | 1.76% |
| 297 | 2,059 | 1,916 | 6.95% | 2,035 | 1.16% |
| 298 | 2,072 | 1,921 | 7.31% | 2,037 | 1.70% |
| 299 | 2,062 | 1,926 | 6.60% | 2,039 | 1.09% |
| 300 | 2,075 | 1,931 | 6.97% | 2,041 | 1.63% |
| 301 | 2,089 | 1,936 | 7.33% | 2,044 | 2.17% |
| 302 | 2,078 | 1,941 | 6.62% | 2,046 | 1.57% |
| 303 | 2,092 | 1,945 | 6.99% | 2,048 | 2.10% |

From the results presented above, it can be observed that, for the temperature range for which experimental data are available, the values obtained using both estimation methods are comparable. Comparing them with the experimental data, the error in the case of the Ceriani method is around 7%, while in the case of the Zong method the error is smaller, being around 2%.

Extrapolating the results on a larger temperature interval, it can be observed from Fig. 2 that the results obtained using the Ceriani method follow the trend of the experimental data, while the results obtained using the Zong method get farther away with the increase of the temperature.

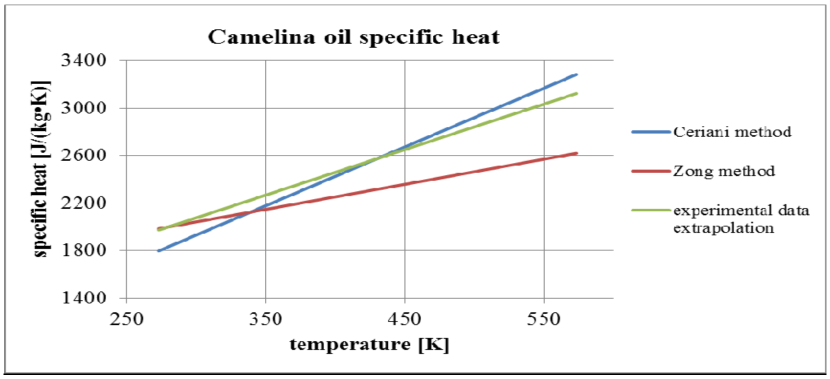


Fig. 2 Specific heat of camelina oil [J/(kmol·K)]

## 6. Thermal conductivity estimation methods

To estimate camelina oil thermal conductivity, two methods have been used: the Sastri-Rao method [6] and the Baroncini method [6].

The calculation formula proposed by the Sastri-Rao method is:

$$k = k_b \cdot \alpha^{\beta} \tag{29}$$

$$k_b = \sum n_i \Delta k_i \tag{30}$$

where:

$$\beta = 1 - \left( \frac{1 - T_r}{1 - T_{br}} \right)^{\gamma} \tag{31}$$

where $n_i$ represents the number of group $i$ in the compound, $\Delta k_i$ is the coefficient specific to each group, $T_r$ is the reduced temperature and $T_{br}$ represents the ratio of the normal boiling point and the critical temperature. The constants α and $\gamma$ have the following values: 0.16, respectively 0.2. The values of the $\Delta k_i$ coefficients used in the calculations are given in reference [6].

The calculation formula proposed by the Baroncini method is:

$$k = A \cdot T_b^{\alpha} \cdot M^{-\beta} \cdot T_c^{-\gamma} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{32}$$

where $M$ represents the molar mass (g/mol), $T_b$ is the normal boiling point, $T_c$ is the critical temperature, $T_r$ is the reduced temperature, and $A$, $\alpha$, $\beta$ and $\gamma$ are constants specific to the method. In the case of esters, these constants have the following values: $A=0.0415$, $\alpha=1.2$, $\beta=1$ and $\gamma=0.167$ [6].

In the case of camelina oil thermal conductivity, experimental data are available only for the temperature of 298 K. Comparing this value with the ones obtained by applying the estimation methods the following errors have resulted.

*Table 10*

**Thermal conductivity of camelina oil k [W/(m·K)]**

| *T[K]* | *Experimental data* | *Sastri-Rao method* | *Error* | *Baroncini method* | *Error* |
|---|---|---|---|---|---|
| 298 | 0.163 | 0.160 | -1.36% | 0.041 | -74.86% |

From the results presented above, it can be concluded that the Sastri-Rao method is better suited for estimating the thermal conductivity of camelina oil at the temperature of 298 K. Since no experimental data are available for other temperatures, the accuracy of the method cannot be assessed for other temperature values.

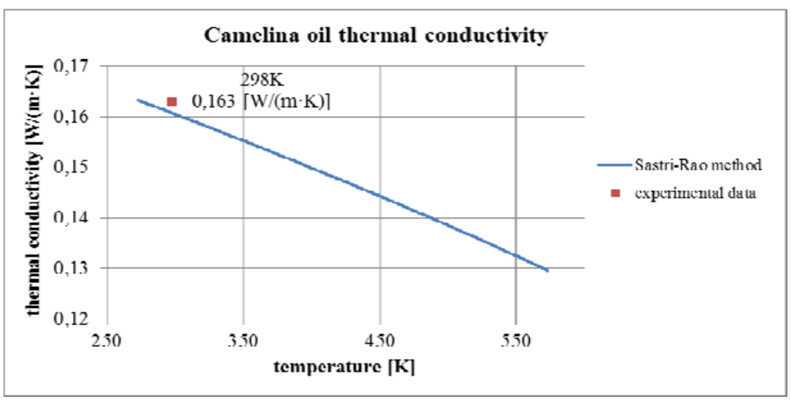


Fig. 3 Thermal conductivity of camelina oil [W/(m·K)]

## 7. Conclusions

In this paper thermophysical properties estimation methods for the particular case of camelina crude oil have been presented. The literature data regarding these properties for the camelina oil is very scarce. Some of the camelina oils properties have been determined experimentally, but not on a very large temperature interval. Being important to know as many as possible properties of camelina oil to better understand its combustion process, mathematical methods have been employed to estimate some of these properties.

In the case of the critical properties of the camelina oil, it has been concluded that the normal boiling point is estimated with the best accuracy by the Banks method, while the critical temperature, pressure and volume are estimated with the best accuracy by the Constantinou & Gani method.

In the case of density, although on the temperature interval for which experimental data is available both presented methods have good accuracy, on a larger temperature range the Zong method is the most accurate.

In the case of the specific heat at constant pressure, on the temperature range for which experimental data is available both methods have comparable errors: the Zong method 12-13%, and the Ceriani method 17-18%. Extrapolating on a larger temperature interval, the results obtained with the Ceriani method follow the trend given by the experimental data, while the results obtained using the Zong method become divergent above a certain temperature.

In the case of the thermal conductivity, data for only one temperature value, 298 K, is available. Two methods have been used to estimate the thermal conductivity corresponding to this temperature value. The best result has been obtained by the Sastri-Rao method, with an error under 2%. Other experimental data not being available, it cannot be said if the results obtained with this estimation method on larger temperature intervals will have the same good accuracy.

The values of the camelina oil thermophysical properties presented in this article are very similar with those of various vegetable oils [13, 19, 20], oils from which biofuels can be obtained. Thus, for the future it is considered to carry out straight camelina oil combustion tests on a heating plant's burner.

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