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Measurement of the nucleation and growth kinetics of some middle distillates fuels and their blends with a model biodiesel fuel

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Abstract

The nucleation kinetics and crystal growth rates of both middle distillates and their blends with a model biodiesel were determined. Being middle distillates complex mixtures of hydrocarbons, a strategy was taken to define the solute and solvent. Different mixtures were prepared from different fuels, and a mixture law was used to calculate the mass percentages of each n-paraffin in the mixture: the difference between experimental and estimated compositions is negligible. An experimental device was set-up to obtain the solubility curve of a distillate, for the first time. The application of the classical homogeneous nucleation theory and the Nývlt's semi-empirical approach allowed to obtain the nucleation rate, interfacial tension and nucleation order. The presence of esters does not have an influence on the solubility curve slope, but they have higher kinetic parameters, and an influence on the interfacial tension. The values found using the Nývlt law are typical for organic systems.

Images were taken as a function of temperature and time, using thermomicroscopy, and image analysis enabled to obtain the crystal growth rates. The mixtures containing esters have in general higher growth rates. The solvent nature plays an important role in the growth, since the other alternative fuels studied have considerably higher growth rates.

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1 ***1. Introduction***

2 During the distillation of crude oil, the cuts from 180° to 360°C provide the so-called
3 middle distillates, which correspond to complex mixtures of hydrocarbon components including
4 saturates, aromatics, resins and asphaltenes. Middle distillates include diesel, heating fuel (FOD)
5 and jet fuel. Even if the characteristics of FOD and diesel are very similar, there are some non-
6 negligible differences: the FOD has higher nucleation temperatures, what can cause filter
7 clogging in case of use in diesel engines; the viscosity of FOD is significantly higher, what can
8 cause problems in the fuel injection system; the final boiling point of FOD is higher, leading to
9 the formation of deposits; the sulfur content in FOD is limited to 2000 ppm; the cetane number
10 of FOD is significantly lower.¹ So, it is not recommended to use the FOD as an alternative to
11 diesel, even if there is a higher tax rate of diesel than home heating oil. Nevertheless, it is still
12 important to compare their behavior and characteristics.

13 The high price of crude oils and the worldwide concern for CO₂ emissions support the
14 production and the use of biofuels, in addition to being chemically less complex than the
15 conventional diesels. The final price of biodiesel and its properties depend upon the fats and oils
16 used in its production. Fatty acid methyl esters (FAME) of lipids such as soybean, rapeseed,
17 canola oils, used cooking oil, waste greases or tallow are the most common used.² Biodiesel from
18 cheap vegetable oils, such as palm oil, with a large concentration of saturated fatty acid esters
19 has a worst performance at low temperatures having tendency to crystallize, even if it is less
20 vulnerable to oxidation and displays better combustion properties.³ A biodiesel has in general
21 higher melting point than a conventional diesel, because it is essentially determined by the
22 amount of saturated esters (which have higher melting points) and does not depend upon the
23 composition of the unsaturated esters (which act essentially as solvent). The presence of crystals

1 in the biodiesel, like in conventional diesels, affects its viscosity, flowability and filterability.⁴
2 Solutions have been proposed in order to overcome the problems with fatty acid esters at low
3 temperatures: the preferred and most widely used is blending biodiesel with conventional diesels.
4 Conventional fuels in blends act as a solvent of precipitated crystals at low temperature which is
5 reflected in improved low temperature properties.⁵

6 As the temperature decreases, the solubility limit of a middle distillate may be reached and the
7 solution will no longer be able to support all the n-paraffins. The solubility limit of the heaviest
8 n-paraffin components is commonly referred as the cloud point (CP), also known as wax
9 appearance temperature (WAT), and it allows to differentiate between products in terms of
10 performance. The problem of crystallization based on flow conditions, pressure and temperature,
11 is transverse to all activities in the oil industry with major economic consequences: production,
12 transportation, refining, formulation of finished products, and the use of fuels. However,
13 deviations from the expected crystallization behaviour may occur caused by the presence of
14 other components in the crystal growth medium. These components, such as aromatics,
15 asphaltenes, resins, water, additives, and shorter chained n-paraffins, can impact a number of
16 factors: crystal morphology, crystal growth rate, nucleation kinetics, crystallization
17 thermodynamics, and dissolution kinetics.⁶

18 Solid formation, impossible at lower concentration than that of the solubility onset at the given
19 temperature and pressure conditions, may take place at a concentration higher than the
20 theoretical solubility level. The difference between the actual value of the solute concentration at
21 the crystallization operating point and the theoretical solubility onset is called supersaturation
22 (S), and is a fundamental factor in crystallization dynamics. Supersaturation is the driving force
23 for both the initial nucleation step and the following crystal growth.

1 The ideal zone for the crystal growth is the metastable zone localized between the solubility
2 and supersaturation curves. The metastable zone width (MSZW) is of major importance in
3 crystallization and depends on: saturation temperature, solvent, impurities or seeds, stirring and
4 cooling rate. Once the MSZW is determined, it is possible to carry out a crystallization process
5 where a constant supersaturation is maintained throughout the cooling, leading to nearly constant
6 nucleation and crystal growth rate.⁷ The polythermal technique is one of the most widely used
7 for determining the MSZW: it involves cooling a solution at a fixed rate until nucleation, and the
8 process is repeated for a variety of rates. Thermal methods are very convenient to evaluate the
9 onset of nucleation or complete dissolution of crystals, and also to provide information about
10 their kinetics. The detection method used has a great influence on the kinetics since there is a
11 time lag between nucleation and a detectable crystal size. The structure of the critical nucleus for
12 a given supersaturation is theoretically impossible to establish and the extent of nuclei growing
13 beyond the critical size previous to detection may strongly depend on the selected method.

14 Saturation temperatures and MSZW were measured for the n-paraffins C₁₈ to C₂₉ and for
15 binary mixtures of C₂₀ and C₂₂ crystallized from n-dodecane and m-xylene solvents by Gerson et
16 al.⁸ The MSZW obtained illustrates the effect of growth environment on the crystallization
17 process. The nucleation kinetics data obtained from induction time measurements show the
18 effect of increasing solute concentration on critical cluster size together with the value of
19 interfacial tension.⁸

20 The main objective of this work is to study the crystallization of n-paraffins in real middle
21 distillates, as well as the impact of alternative fuels. For that, it was proposed to expand the
22 analytical devices used for monitoring crystallization, and to rely on models of crystallization
23 kinetics. Crystallization studies of middle distillates were carried out using the polythermal

1 method using turbidimetry to detect the nucleation onset and dissolution end. Thermal-optical
2 microscopy was used to study the crystal growth, and to link the thermal effects to the
3 morphological changes.

4

5 **2. Theory**

6 From a thermodynamic point of view, the wax formation consists in a solid-liquid equilibrium
7 where the n-paraffins act as solutes and all the other compounds as solvents.⁹⁻¹¹ Ideally, at a
8 given temperature, the solute should include all the species which, in the pure state, have a
9 melting point higher or equal to that temperature.¹²⁻¹³ The considered solvent is a typical one that
10 mimics the paraffin based, aromatic and oil-like solvents, and does not crystallize at the studied
11 temperatures.

12 Several theories have been introduced to rationalize the nucleation and growth kinetics,
13 however the complexity of the process and experimental limitations difficult their application to
14 data analysis in most cases. Therefore, empirical approaches are most often preferred to analyse
15 the crystallization kinetics, most of them initially based on the classical nucleation theory.¹⁴

16

17 **2.1 Solubility**

18 The saturation curve and metastable zone width are essential tools since the shape of the
19 solubility curve defines the crystallization mode and the supersaturation conditions. The
20 solubility curve, representing the equilibrium curve (equilibrium temperature vs concentration
21 percentage of solute in solution), should be independent of the heating rate. However, the heating
22 rate will influence the supersaturation and therefore the kinetics and MSZW. If the dissolution
23 temperature is plotted against the heating rate for different mixtures which have the same solvent

1 but different solute concentration, the best straight lines through these points could be
2 extrapolated to zero. This will allow to obtain the saturation temperatures at an infinitesimally
3 small rate of temperature change, and like that the equilibrium curve (solubility).^{7,8}

4 If the log of the solubility, in mole fraction (x), is plotted against the inverse of the absolute
5 temperature (T), the dissolution enthalpy (ΔH_{diss}) and entropy (ΔS_{diss}) can be determined by
6 fitting the solubility data to the van't Hoff equation, assuming ideal behaviour and negligible
7 heat capacity difference between the solute and the solvent.^{15,16}

$$8 \quad \ln x = -\frac{\Delta H_{dissolution}}{RT} + \frac{\Delta S_{dissolution}}{R} \quad (1)$$

9 where R is the ideal gas constant. The van't Hoff equation provides a robust thermodynamic
10 model for single-components dissolved in organic solvents at low mass fractions. When applied
11 to polydisperse distributions, significant uncertainty may exist in the solubility because only
12 the highest paraffins contribute to the crystal, while the other components remain in the liquid
13 phase at the nucleation point. For the scope of this work, this approximation can be acceptable,
14 but a better approximation of solubilities could be obtained from the general solid-liquid
15 equilibrium equation that relies on the composition of solute in solid and liquid phases.^{9,17,18}

16

17 **2.2 Classical Homogeneous Nucleation Theory**

18 The kinetics of paraffin gel formation was studied by Paso et al.¹⁵ using model fluids
19 consisting of monodisperse and polydisperse n-paraffin components dissolved in petroleum
20 mineral oil. Even if in the majority of industrial applications is the heterogeneous primary
21 nucleation that dominates (almost inevitable presence of pollution and insoluble), these authors
22 considered that for simple model fluids, the nucleation mechanism is homogeneous. The
23 homogeneous nucleation of n-paraffins constitutes a special case which occurs spontaneously

1 and randomly throughout the bulk melt, and is not initiated by any extrinsic agents such as
2 surfaces or impurities.¹⁹ So, the same will be considered for real systems, complex multi-
3 component hydrocarbon fuels, in order to apply the classical homogeneous nucleation theory.

4 The main equations related to the homogeneous nucleation theory can be found elsewhere.⁷

5 The supersaturation (S) definition in mole fraction is given by:

$$6 \quad \ln S = \frac{\Delta H_{diss}}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right) \quad (2)$$

7 where T_s is the saturation temperature. Paso et al.¹⁵ defined the working equation for
8 correlating the classical homogeneous nucleation theory with the experimental measured
9 nucleating points expressed as ΔT (difference between the dissolution and nucleation
10 temperatures, also known as metastable zone width):

$$11 \quad \frac{A}{\rho^*} \Delta T \left[\exp\left(-\frac{B}{\Delta T^2}\right) - \frac{\sqrt{B\pi}}{\Delta T} \operatorname{erfc}\left(\frac{\sqrt{B}}{\Delta T}\right) \right] = \beta \quad (3)$$

12 where β is the cooling rate. The values of B and $\frac{A}{\rho^*}$ are fitting parameters obtained by least-
13 squares minimization procedure. Knowing B and ν , the value of interfacial tension γ can be
14 estimated.

15

16 **2.3 Nývlt Law**

17 If the considered section of the metastable zone is not too large, it is reasonable to suppose that
18 the saturation and supersaturation lines are linear and parallel, and consequently the nucleation
19 rate equals the rate of solution supersaturation, at least when nucleation is detected. Combining
20 these hypotheses to the principles of the homogeneous nucleation rate:

1
$$\log \Delta T = \frac{1-n}{n} \log \frac{dC^*}{dT} - \frac{1}{n} \log k_n + \frac{1}{n} \log \beta \quad (4)$$

2 According to this equation, commonly known as Nývlt's approach,²¹ the representation of
3 $\log(\Delta T)$ against $\log \beta$ will render a straight line which slope and intercept are related to the
4 nucleation order n and the rate constant of the crystallization k_n , respectively. n describes the
5 dependence of the nucleation rate to the supersaturation (potential of a solute/solvent system to
6 nucleate quickly); k_n describes the dependence of the nucleation kinetics on the solute nature (a
7 solute which has a higher intrinsic nucleation kinetics will have a higher k_n). For organic
8 crystallizing systems, the value of the nucleation order (n) is typically between 5 and 10.^{16,20}

9 In spite of some severe underlying approximations, for industrial applications, this is a simple
10 and useful way of characterizing systems and their crystallization kinetics based in a material
11 balance made in a closed mixed vessel where the supersaturation is assured by cooling.²¹

12

13 **2.4 Growth kinetics**

14 A basic expression is used to express the relationship between supersaturation and crystal
15 growth:

16
$$G = k_G \Delta C^g \quad (5)$$

17 where G is the linear crystal growth rate (length/time) and, g is the crystal growth apparent
18 order (temperature-dependent) and is normally a number between 1 and 2.⁷ There are a number
19 of experimental methods that can be used to obtain the crystal growth rate data needed to obtain
20 kinetics, such as induction time measurements²² or droplet based microfluidic²³.

21

1 **3. Materials and Methods**

2 **3.1 Materials**

3 In this work, three types of fuels with different distillation ranges and paraffin levels (heavy,
4 light, and distillate hydrocracker (DHC)) are used to prepare different diesels (B0). Table 1
5 shows the characteristics of each one, as well as those of the heating fuels studied (FOD1 and
6 FOD2) for comparison. To prepare different blends of 7%vol ester in the middle distillates (B7),
7 esters from different sources are mixed, and their nature and quantity are reported in Table 2.

8 Two standard mixtures were prepared from the original fuels, B0 and B7, and from them,
9 several other mixtures were prepared with different percentages of fuels, keeping the solvent
10 constant (aromatics, naphthenes,...) but changing the n-paraffins mass percentage and their
11 paraffinic profile. The mixtures are denominated from B0 to B0 8, and from B7 to B7 6 for the
12 mixtures containing esters (FAME). The compositions of these mixtures were calculated by a
13 weighted average, considering the composition of each original fuel and the formulation of each
14 mixture. The n-paraffin content of each mixture is presented in Table 3.

15

16 **3.2 Nucleation experimental set-up**

17 The crystallization reactor consists in a triple-wall jacketed 50cm³ glass vessel which has ports
18 to accommodate the turbidity and temperature probes. A magnetic stirrer (IKA-WERK ES5) is
19 used to agitate the solution where a speed of 400 rpm is applied which ensures an adequate
20 mixing and avoids excessive splashing in the vessel. Cooling and heating programmes are
21 implemented using a cryothermostat (LAUDA Kryomat RUK 90S). Temperature data are
22 recorded using a Pt100 resistance probe which is immersed in the solution and is connected to
23 the cryothermostat.

1 The turbidity probe introduces light into the reactor from a light source (Avantes AvaLight
2 DHS) and collects the dispersed light which is then analysed (Avantes Multichannel
3 Spectrophotometer). A fiber optics system connects the probe to the light source and
4 spectrophotometer. In this work, the scattered light intensity was analysed in the wavelength
5 range between 450 and 655 nm.

6 The crystallization reactor is initially loaded with approximately 20 cm³ of the sample, and
7 stirring is started at the desired rate (400 rpm). The solution is first heated until 35°C to ensure
8 complete dissolution and minimize memory effects. The solution is then cooled, at a fixed
9 cooling rate, until a temperature just below the appearance of the first crystals. The formation of
10 crystals is accompanied by a rapid increase of the scattered light intensity. Then, a heating ramp
11 is imposed, at the same rate used in the cooling, until complete dissolution (35°C). The value at
12 which the scattered light intensity increases is taken as the nucleation temperature, while that at
13 which it decreases, is taken as the “equilibrium” saturation temperature (dissolution). The
14 procedure is repeated for different cooling/heating rates (2, 10, 30 and 60°C/hr), and at least
15 three measurements are done at each rate. To minimize the amount of sample consumed, the
16 same solution is recycled batch to batch.

17

18 **3.3 Thermomicroscopy**

19 A microscope (LEICA DM RXA) equipped with a polarized light and a phase contrast device
20 was used. It is connected to a hot stage (Linkam Optical DSC600), which can operate in the
21 range from -150 to 600°C controlled by a cooling system (LNP95). The heat/cooling rates are
22 limited to 6 to 1800°C/hr, with a precision of 0.01°C. Images are acquired using a sensitive
23 charge-coupled device colour camera (PCO Sensicam QE).

1 The solution is placed in a quartz crucible (15mm diameter and 20 μ l), and a cooling rate is
2 imposed, without any stirring. Image acquisition is done simultaneously. The linear growth rate
3 can be obtained by measuring the largest crystal dimension (the width) as a function of time (and
4 temperature). A standard cooling rate of 0.5°C/min is used and at least ten crystals are followed
5 to study the crystal growth rate.

6

7 **4. Results and Discussion**

8 When cooling a diesel (B0), the solute is considered to be the n-paraffins while the other
9 components constitute the solvent. In the case of mixtures diesel/FAME (B7), the saturated
10 esters are considered as solute as well. The solvent includes: isoparaffins, naphthenes, iso-
11 naphthenes, di-naphthenes, mono-, di-, tri- and poly-aromatics, monoaro- and diaro-naphthenes,
12 and a mass percentage lower than 0.1% of other components, as showed in Table 1 for the
13 different fuels.

14 As mentioned before, several different mixtures were prepared from different fuels. A mixture
15 law was used to calculate their composition: knowing the density, volume percentage and
16 composition of pure fuels, and the formulation of the mixture, its composition can be calculated.
17 Experimental data of the composition of each mixture was compared to the estimated values, and
18 the standard deviations are negligible: considering the n-paraffins, the standard deviation is in
19 average 2.42% which can be considered a very good agreement.

20 The molecular weight (M) of each mixture was calculated by a weighted average considering
21 the estimated mixture composition and the molecular weight of each component. From the
22 density of each fuel and the formulation of each mixture, the mixture density (ρ) was estimated.
23 Knowing M and ρ , the molar volume (v) was estimated. These values together with the

1 concentration of n-paraffins are presented in Table 3, and they are in good agreement with
2 available literature values.²⁴ The values of M , ρ and ν are quite similar for all the studied
3 mixtures, even if the quantity of n-paraffins and their profile are changed.

5 **4.1 Blends diesel/biodiesel and heating fuels**

6 The nucleation, T_n , and dissolution, T_s , temperatures were measured for the different mixtures,
7 and the respective differences (ΔT) are presented in Figure 1 and Figure 2, respectively for
8 diesels and biodiesels. These values are averages of at least three different measurements, and
9 the standard deviation in the absolute temperatures ranges between 0 and 11%. As expected, the
10 dissolution temperature is always higher than that of nucleation, and the difference between them
11 is higher at the highest rates. However, in both nucleation and dissolution, the rate has not a great
12 effect, and they can be considered almost constant as a function of cooling/heating rate. Initially,
13 seven different rates were tested, but as it was found that the rate has not a remarked effect, only
14 four rates were studied for the other samples. Turnbull and Cormia²⁵ showed that from C_{16} to C_{32}
15 the relative undercooling for homogeneous nucleation, $\Delta T/T_s$, is ~ 0.04 instead of the ~ 0.2
16 common to most organic materials. The samples studied in this work have $\Delta T/T_s$ between 0.008
17 and 0.013, which means that in the case of real systems the maximum undercooling is lower than
18 for model systems.

19 These diesels are mixtures of three different fuels, and highest the ratio light to heavy, lower
20 the nucleation and dissolution temperatures, as in the cases of B0 5, B0 8, B7 3 and B7 5 where
21 the quantity of light fuel is especially high. The quantity of DHC also plays an important role:
22 higher it is, higher the temperatures, as in the case of B0 7 where the same quantity of heavy and
23 DHC is used.

1 The values obtained for the standard B0 are in good agreement with the commonly found for
2 traditional diesels.^{3,26} In addition, the type of curves found are similar to those found for model
3 systems like octacosane/toluene, but with very different dissolution and nucleation temperatures.
4 Comparing the nucleation temperatures of the mixtures B7, with values available in the literature
5 for traditional biodiesels,^{4,27} it can be seen that the blends diesel/esters prepared in this work have
6 better cold flow properties (lower cloud points).

7 Comparing the mixtures based on B0 and the corresponding B7 (it means that the quantity of
8 light and DHC fuels are the same), it can be seen that the temperatures are in the same range, as
9 well as the order by which the samples are classified: for example, B0 5 and B7 3 are the ones
10 with lower nucleation and dissolution temperatures; while B0 2 and B7 2 have the higher. This
11 means that the quantity of esters has almost no influence on the nucleation, being the n-paraffin
12 quantity the major parameter playing a role. This was kind expected since in Table 3 it can be
13 seen that the esters had a maximum total saturated FAME content of 12% which means that
14 blending the middle distillates with 7%vol esters meant that the total saturated FAME content
15 was less than 1%, in any of the blends.

16 The heating fuels (FOD1 and FOD2) have considerable worst cold flow properties: from 1.4
17 and -0.4°C for the nucleation temperature; and from 3.40 to 2.55 for the dissolution. The final
18 distillation temperature of a FOD is higher than that of a conventional diesel: this means that
19 there are more dissolution of the lighter paraffins and so the heavier will be more concentrated in
20 FOD, causing problems in cold temperature behaviour. The paraffins distribution in FOD is
21 bimodal and centred between C₁₁ and C₁₇, while for the conventional diesels is centred in C₁₆.
22 The amount of n-paraffins is higher in a conventional diesel but especially rich in light paraffins
23 which crystallize at lower temperatures what will make the nucleation temperature to be lower.

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4.3 Effect of concentration

The solubility curves, expressed in concentration of solute, are shown in Figure 3, for the mixtures based in B0 and for those based in B7. This is the first time that the solubility curve is measured for that kind of complex systems. It should be focused that the difference on the solubility curve slopes between B0 and B7 is negligible and so the esters have a slightly effect on the solubility slopes.

The concentrations in g/100g were converted in mole fraction considering the molecular weight of solute and solvent. This allowed the application of the empirical van't Hoff approach even if this corresponds to a great simplification. The results of the dissolution properties are presented in Table 4: the difference between B0 and B7 values are negligible, as expected since the same was seen in the solubility slopes.

If the obtained values are compared with literature values for model systems, like monodisperse and polydisperse *n*-paraffins dissolved in mineral oil^{4, 15} for real systems the values are lower: the quantity of components in the solute and the solvent makes the interactions to be weaker and so, the quantity of energy needed to broke them is lower. The dissolution enthalpy is associated with the dissolution of a substance in a solvent at constant pressure resulting in infinite dilution. The energy change can be regarded as the endothermic breaking of bonds within the solute and within the solvent, followed by the formation of attractions between the solute and the solvent. So, these values are very dependent on the solute and solvent interactions.

1 **4.4 Nucleation kinetics**

2 Applying the equations presented in section 2.2, to relate the critical undercooling measured
3 through a polythermal approach as a function of cooling rate, an estimation of the crystal-
4 solution interfacial tension was done which is considered as crystal face and temperature
5 independent. The values of B and A/ρ^* are obtained for each cooling rate, and the standard
6 deviation between them was lower than 5%. So, another minimization was done of all the least-
7 squares corresponding to a mixture, and fixed B and A/ρ^* for a given mixture were obtained.
8 This led to a single interfacial tension, cooling rate independent, presented in Table 3. The
9 supersaturation presented is that estimated at 1°C/min because this is the common rate used for
10 the measurements of the filtering limit temperature. The presence of FAMEs makes the
11 supersaturation at nucleation and the interfacial tension to increase, as well as the critical radius
12 and consequently the Gibbs energy. The composition of the mixtures changed, including the
13 saturated, aromatic, resin and asphaltenes fractions. And so, the interactions between the polar
14 functional groups are changed which are important to its structure and characteristics.

15 It is known that the constraints on the liquid chains connected to the critical nucleus yield an
16 entropic cost and, therefore, an increase of the interfacial tension.²⁸ Kraack et al.¹⁹ estimated the
17 solid-liquid interfacial tensions of *n*-paraffins from 17 to 60 dyn/cm, and the values found in this
18 work are considerably lower than theirs. Gerson et al.⁸ determined the interfacial tension from
19 the induction time of docosane crystallized from dodecane and the values are lower than the
20 found in this work, even if in the same order. The same happens in comparison to the values
21 determined by Paso et al.¹⁵ for monodisperse C₃₆ and C₃₅ and polydisperse *n*-paraffin
22 components dissolved in petroleum mineral oil.

23 Three main variables govern the nucleation rate: temperature; supersaturation; and interfacial
24 tension. The values of supersaturation and interfacial tension were presented in Table 3. In the

1 impossibility of performing molecular simulations to establish the nuclei structure, a constant A
2 value equal to 10^{30} nuclei/cm³.s was considered.²⁰ Consequently, the nucleation rate was
3 calculated and represented as a function of supersaturation. As shown in Figure 4a, there is an
4 extremely rapid increase in the nucleation rate for B0 once some critical supersaturation level is
5 exceeded, being the one with higher nucleation rates. It can be seen that to obtain the same
6 nucleation rate, higher supersaturation is required in the cases of B7 and FOD when compared to
7 B0, which means lower temperatures and better flowability. This means that for B7 and FOD be
8 used in the same conditions as B0, some additives should be added.

9 This can be ensured if a comparison is made between the mixtures prepared from B0 and the
10 corresponding from B7. The first have higher nucleation rates, and so higher number of nucleus
11 per unit of volume and time, than the corresponding mixtures prepared from B7 (Figure 4b).
12 Those mixtures have exactly the same quantity of heavy and DHC fuels, being the quantity of
13 light fuel slightly lower in the B7 mixtures given that they are blended with 7%vol of esters. It
14 clearly appears from these figures that the presence of alternative fuels lengthens the nucleation
15 rate.

16 The previous analytical approach based on the classical nucleation theory allowed to obtain a
17 characteristic parameter of the interactions crystal-solution. Even if the nucleation rate was also
18 obtained using this approach, another empirical approach was used to describe nucleation
19 kinetics, the Nývlt law (section 2.3). The application of equation (4) leads to two empirical
20 parameters, n and k_n , and the first aim of its application is to determine those values, considering
21 the solubility curve slopes presented in Figure 3. The uncertainties in the solubility curves slopes
22 are so low that they have no effect on the kinetic parameters presented in Table 3. For the
23 mixtures studied in this work, the behaviour is similar to conventional organic systems, given

1 that n is between 5 and 10, including those of the studied FODs. In general, the kinetic
2 parameters in the presence of FAMEs are higher. In general, the lower the solubility of a solute
3 in a given solvent, the higher is the value of n , and higher the nucleation temperature. This means
4 that it is a useful parameter to assess the effect of different solvents or solvent compositions on
5 the metastability of a solution: given that in the presence of FAME it is higher, this means that
6 those mixtures have higher nucleation temperatures, and consequently the applicability of those
7 fuels is not possible unless some cold behaviour treatment is applied.

8 It should be mentioned that for the FODs the same solubility curve as B0 was considered, as
9 well as the molecular volume and dissolution enthalpy. This can cause deviations from the real
10 behavior, and the obtained results with models for FOD are just for comparison.

11

12 **4.5 Experimental Growth Rate**

13 Claudy and Letoffé^{29,30} used optical microscopy in polarized light to study the crystallization
14 of n-paraffins in middle distillates and they concluded that it is the most appropriate mode to
15 observe paraffin crystallization. The crystals obtained in this work are plate-like with a high
16 aspect ratio and a lozenge shape. Images of three different samples are presented in Figure 5.

17 The linear crystal growth rate was measured for each different mixture based on at least ten
18 different crystals, and the results are presented in Table 3, together with the crystal size (width,
19 L) a time delay after nucleation (30-50s). Experimentally it was seen that the presence of FAMEs
20 has not a remarked effect on the crystal size but generally increases the crystal growth rate. The
21 nature of the solvent plays an important role in the growth, since the FODs have considerably
22 higher growth rates.

1 At low supersaturation, crystals can grow faster than they nucleate resulting in a bigger crystal
2 size and narrow crystal size distribution. However, at higher supersaturation, crystal nucleation
3 dominates crystal growth, ultimately resulting in smaller crystals and broad crystal size
4 distribution. As seen before, the FODs have lower supersaturation at nucleation than the other
5 mixtures, and here it was found that they have higher growth rates as well as bigger crystals. In
6 opposition, B0 have a slightly higher supersaturation at nucleation, and a lower growth rate as
7 well as smaller crystals.

8 Considering a metastable zone sufficiently thin that the saturation and supersaturation curves
9 are linear and parallel and the growth predominates over nucleation, the supersaturation is
10 converted in temperature difference. So, if the linear growth rate was measured at different
11 cooling rates, and consequently the ΔT estimated, the values of k_G and g can be obtained by
12 linearization of equation (5). The results for B0 and B7 are presented in Table 5 where it could
13 be seen that the growth rate increases when the cooling rate increases. However, the maximal
14 size of the crystals is almost not affected. The growth order g increases with the growth rate and
15 also with the metastable zone width. As mentioned before, for common organic systems the
16 value of g should be between 1 and 2 what means that B0 and B7 can be considered as common
17 organic systems.

18

19 **5. Conclusions**

20 The aim of this work was to study crystallization kinetics for middle distillates, in order to
21 better understand their cold flow behaviour. Firstly, a mixture law was used to calculate the
22 paraffin contents of a mixture based on those of its constituting fuels. The concentration of
23 interest will be those of n-paraffins ($10 < C < 50$ g/100g) and, concerning these species the standard

1 deviation between measured and estimated concentrations is 3.2% which corresponds to a very
2 good agreement. The solute was defined as the n-paraffins and the saturated esters; all the other
3 components (naphthenes, asphaltenes, aromatics) were considered as solvent. Different
4 mixtures were prepared from two standard mixtures, keeping the solvent and changing the
5 paraffins mass percentage and their paraffinic profile.

6 An experimental device was set-up to measure dissolution and nucleation temperatures and it
7 was verified that the cooling/heating rate has a negligible effect on the nucleation/dissolution
8 temperatures. Solubility curves were obtained for the first time for such complex systems. It was
9 seen that the esters have no influence on the solubility, but if the nature and source of esters are
10 different the effects can be different. The uncertainty of the solubility curve slopes is so small that
11 there is no effect on the kinetic parameters.

12 The application of the homogeneous nucleation theory allow to calculate the nucleation rate as
13 a function of the supersaturation what show that concerning the nature of the sample the
14 nucleation will be different. The interfacial tension between crystal and solution for the different
15 studied samples was obtained what allows distinguishing between samples. The Nývlt law was
16 applied to obtain the kinetic parameters, and it was seen that the order of nucleation is similar for
17 all the studied samples and they could be considered as normal organic systems. The
18 applicability of some studied mixtures as fuels will be possible just in case of cold flow treatment
19 for example with some additives.

20 A second experimental device was introduced to study the crystal growth rate. All the studied
21 samples have crystals of the same shape (plate-like) only changing the size and the
22 supersaturation at nucleation. The linear crystal growth rate changes concerning the nature of the

1 sample. A kinetic growth rate law was obtained for samples with and without esters, being the
2 apparent order of growth higher in the absence of esters.

3

4 ***Nomenclature***

5	A	pre-exponential factor or collision factor
6	B	fitting parameter
7	g	crystal growth apparent order
8	G	overall linear growth rate
9	J	nucleation rate
10	k_n	nucleation rate constant
11	k_G	growth rate constant
12	L	characteristic size of the crystal
13	M	molecular weight
14	n	apparent order of nucleation
15	r	radius
16	R	ideal gas constant
17	S	supersaturation
18	T	temperature
19	v	molar volume
20	x	solubility, in mole fraction
21		
22	<i>Greek letters</i>	
23	β	cooling rate
24	γ	interfacial tension
25	ρ	density of the mixture can be estimated
26	ρ^*	critical nuclei number density (fitting parameter)
27	ΔC	MSZW for a given temperature (in mass of solute per mass of solvent)
28	ΔH	enthalpy
29	ΔS	entropy

1 ΔT maximum undercooling
2 $\Delta T/T_s$ normalized metastable zone

3

4 *Subscripts*

5 *c* *critical*
6 *diss* dissolution
7 *s* dissolution
8 *n* nucleation

9

10 *Abbreviations*

11 *B0* diesel
12 *B7* mixture diesel/biodiesel
13 *CP* cloud point
14 *DHC* fuel coming from new refinery schemas
15 *FAME* fatty acid methyl esters
16 *FOD* heating fuels
17 *MSZW* metastable zone width

18

19 ***References***

20 (1) Papin, G. Synthèse, caractérisation et évaluation de nouveaux additifs de tenue à froid des
21 gazoles et fiouls domestiques, Bordeaux; 2008.

22 (2) Dunn, R.O. Crystallization behavior of fatty acid methyl esters. *Journal of the American*
23 *Oil Chemists Society* **2008**, 85, 961-972.

24 (3) Knothe, G.; Dunn, R.O. A Comprehensive Evaluation of the Melting Points of Fatty Acids
25 and Esters Determined by Differential Scanning Calorimetry. *Journal of the American Oil*
26 *Chemists Society* **2009**, 86, 843-856.

- 1 (4) Lopes, J.C.A.; Boros, L.; Krahenbuhl, M.A.; Meirelles, A.J.A.; Daridon, J.L.; Pauly, J.;
2 Marrucho, I.M.; Coutinho, J.A.P. Prediction of cloud points of biodiesel. *Energy & Fuels* **2008**,
3 *22*, 747-752.
- 4 (5) Sarin, A.; Arora, R.; Singh, N.P.; Sarin, R.; Malhotra, R.K.; Kundu, K. Effect of blends of
5 Palm-Jatropha-Pongamia biodiesels on cloud point and pour point. *Energy* **2009**,*34*, 2016-2021.
- 6 (6) Senra, M.; Paracharoensawad, E.; Scholand, T.; Fogler, H.S. Role of a Carboxylic Acid on
7 the Crystallization, Deposition, and Gelation of Long-Chained n-Alkanes in Solution. *Energy &*
8 *Fuels* **2009**, *23*, 6040-6047.
- 9 (7) Mullin, J.W. Crystallization, Fourth ed., Oxford, Butterworth-Heinemann, 2001.
- 10 (8) Gerson, A.R.; Roberts, K.J.; Sherwood, J.N.; Taggart, A.M.; Jackson, G. The Role of
11 Growth Environment on the Crystallization of Normal Alkanes in the Homologous Series from
12 C18h38 to C29h60. *Journal of Crystal Growth* **1993**, *128*, 1176-1181.
- 13 (9) Coutinho, J.A.P.; Goncalves, C.; Marrucho, I.M.; Pauly, J.; Daridon, J.L. Paraffin
14 crystallization in synthetic mixtures: Predictive local composition models revisited. *Fluid Phase*
15 *Equilibria* **2005**, *233*, 28-33.
- 16 (10) Coutinho, J.A.P.; Mirante, F.; Ribeiro, J.C.; Sansot, J.M.; Daridon, J.L. Cloud and pour
17 points in fuel blends. *Fuel* **2002**, *81*, 963-967.
- 18 (11) Daridon, J.L.; Pauly, J.; Coutinho, J.A.P.; Montel, F. Solid-liquid-vapor phase boundary
19 of a North Sea waxy crude: Measurement and modeling. *Energy & Fuels* **2001**,*15*, 730-735.
- 20 (12) Coutinho, J.A.P. Predictive UNIQUAC: A new model for the description of multiphase
21 solid-liquid equilibria in complex hydrocarbon mixtures. *Industrial & Engineering Chemistry*
22 *Research* **1998**, *37*, 4870-4875.

- 1 (13) Dauphin, C.; Daridon, J.L.; Coutinho, J.A.P.; Baylere, P.; Potin-Gautier, M. Wax content
2 measurements in partially frozen paraffinic systems. *Fluid Phase Equilibria* **1999**, *161*, 135-151.
- 3 (14) Nývlt, J. Kinetics of nucleation in solutions. *Journal of Crystal Growth* **1968**, *3-4*, 377-
4 383.
- 5 (15) Paso, K.; Senra, M.; Yi, Y.; Sastry, A.M.; Fogler, H.S. Paraffin polydispersity facilitates
6 mechanical gelation. *Industrial & Engineering Chemistry Research* **2005**, *44*, 7242-7254.
- 7 (16) Ashbaugh, H.S.; Radulescu, A.; Prud'homme, R.K.; Schwahn, D.; Richter, D.; Fetters,
8 L.J. Interaction of paraffin wax gels with random crystalline/amorphous hydrocarbon
9 copolymers. *Macromolecules* **2002**, *35*, 7044-7053.
- 10 (17) Coutinho, J.A.P.; Daridon, J.L. Low-pressure modeling of wax formation in crude oils.
11 *Energy & Fuels* **2001**, *15*, 1454-1460.
- 12 (18) Coutinho, J.A.P.; Knudsen, K.; Andersen, S.I.; Stenby E.H. A local composition model
13 for paraffinic solid solutions. *Chemical Engineering Science* **1996**, *51*, 3273-3282.
- 14 (19) Kraack, H.; Sirota, E.B.; Deutsch, M. Measurements of homogeneous nucleation in
15 normal-alkanes. *Journal of Chemical Physics* **2000**, *112*, 6873-6885.
- 16 (20) Myerson, A.S. Handbook of Industrial Crystallization 2ed., Woburn, MA, 2002.
- 17 (21) Nývlt, J. The Kinetics of industrial crystallization, New York, 1985.
- 18 (22) Teychené, S.; Biscans, B. Nucleation Kinetics of Polymorphs: Induction Period and
19 Interfacial Energy Measurements. *Crystal Growth & Design* **2008**, *8*:1133-1139.
- 20 (23) Teychené, S.; Biscans, B. Crystal nucleation in a droplet based microfluidic crystallizer.
21 *Chemical Engineering Science* **2012**, *77*:242-248.
- 22 (24) Mesquita, F.M.R.; Feitosa, F.X.; Santiago, R.S.; de Sant'Ana, H.B. Density, Excess
23 Volumes, and Partial Volumes of Binary Mixtures of Soybean Biodiesel plus Diesel and

- 1 Soybean Biodiesel plus n-Hexadecane at Different Temperatures and Atmospheric Pressure.
2 *Journal of Chemical and Engineering Data* **2011**, 56:153-157.
- 3 (25) Turnbull, D.; Cormia, R.L. Kinetics of Crystal Nucleation in Some Normal Alkane
4 Liquids. *The Journal of Chemical Physics* **1961**, 34:820-831.
- 5 (26) Gimzewski, E.; Audley, G. Monitoring Wax Crystallization in Diesel Using Differential
6 Scanning Calorimetry (Dsc) and Microcalorimetry. *Thermochimica Acta* **1993**, 214:149-155.
- 7 (27) Coutinho, J.A.P.; Goncalves, M.; Pratas, M.J.; Batista, M.L.S.; Fernandes, V.F.S.; Pauly,
8 J.; Daridon, J.L. Measurement and Modeling of Biodiesel Cold-Flow Properties. *Energy & Fuels*
9 **2010**, 24:2667-2674.
- 10 (28) Kraack, H.; Deutsch, M.; Sirota, E.B. n-alkane homogeneous nucleation: Crossover to
11 polymer behaviour. *Macromolecules* **2000**, 33:6174-6184.
- 12 (29) Claudy, P.; Letoffe, J.M.; Bonardi, B.; Vassilakis, D.; Damin, B. Interactions between N-
13 Alkanes and Cloud Point Cold Filter Plugging Point Depressants in a Diesel Fuel - a
14 Thermodynamic Study. *Fuel* **1993**, 72:821-827.
- 15 (30) Létoffé, J.M.; Claudy, P.; Kok, M.V.; Garcin, M.; Volle, J.L. Crude Oils -
16 Characterization of Waxes Precipitated on Cooling by Dsc and Thermomicroscopy. *Fuel* **1995**,
17 74:810-817.
- 18

1

2 **Table 1.** Original fuel characteristics.

	Heavy	Light	DHC¹	FOD 1²	FOD 2
Viscosity (mm²/s)	2.629	1.216	4.916		
Density (kg/m³)	831.7	807.6	837.0	860.9	858.0
Flash point (°C)	61	45	113	64	63
Cloud point (°C)	-7.0	-34.0	5.0	0	-1
Paraffin	%m/m				
n-Paraffins	21.54	16.73	15.39	11.15	13.06
Isoparaffins	24.14	27.71	31.56		
Naphthenes	3.76	3.66	4.31		
Isonaphthenes	15.13	19.07	20.34		
Dinaphthenes	6.45	8.61	6.22		
Monoaromatics	12.00	14.37	9.71		
Diaromatics	4.26	1.54	2.60		
Triaromatics	0.61	0.06	0.47		
Polyaromatics	0.09	0.00	0.49		
Monoaromaphthenes	9.97	7.99	7.68		
Diaromaphthenes	2.05	0.27	1.08		
Others	0.00	0.00	0.13		

3 ¹DHC, fuel coming from new refinery schemas; ²FOD, heating fuel

4

1 **Table 2.** FAME analysis of the oil used to prepare B7.

Fatty acid ester		m/m
		%
Palmitic acid	16:0	9.4
Palmitoleic acid	16:1	0.3
	17:1	0.1
Stearic acid	18:0	2.1
Oleic acid	18:1	56.4
Linoleic acid	18:2	20.3
Linolenic acid	18:3	8.6
Arachidic acid	20:0	0.5
Gondoic acid	20:1	1.1
Behenic acid	22:0	0.3
Erucic acid	22:1	0.2
Lignoceric acid	24:0	0.1
Nervonic acid	24:1	0.1
Non identified		0.6

2

3

4

5

1
2 **Table 3.** Solution properties, fundamental nucleation parameters, crystal size and linear growth
3 rate of the different mixtures.

	C_{n-} <i>paraffins</i> (g/100g)	M (g/mol)	ρ (kg/m ³)	v (dm ³ /mol)	T_s (°C)	$S_{1^\circ C/min}$	γ (dyn/cm)	r_c (Å°)	n	$\log(k_n)$	L (µm)	G (µm/s)
B0	18.88	201.89	825.53	0.245	-3.74	1.22	0.89	9.97	7.50	11.3	100	0.69
B0 2	19.35	206.72	827.94	0.250	-4.17	1.21	0.77	9.05	10.0	16.4	86	0.68
B0 4	18.41	197.09	823.16	0.239	-2.63	1.12	0.39	7.14	7.25	11.7	371	6.37
B0 5	17.02	177.55	814.42	0.218	-9.29	1.19	0.99	11.68	10.9	17.7	451	5.38
B0 7	17.93	209.84	826.06	0.254	-1.49	1.17	1.28	18.99	8.16	13.1		
B0 8	17.43	187.11	818.30	0.229	-7.17	1.22	0.95	9.88	7.69	11.8	258	2.62
B7	18.68	201.74	829.07	0.243	-2.69	1.26	0.93	8.68	12.6	19.1	85	2.34
B7 2	19.19	206.32	831.48	0.248	-2.74	1.20	0.81	10.26	12.7	20.5	172	3.83
B7 3	16.67	180.41	817.96	0.221	-9.49	1.31	1.16	8.59	7.67	11.9	50	1.47
B7 4	18.39	199.45	827.96	0.241	-3.50	1.14	0.40	6.54	8.42	13.4	235	12.34
B7 5	17.12	187.72	821.84	0.228	-7.08	1.21	1.01	11.03	9.50	15.1	108	4.98
B7 6	18.16	197.11	826.66	0.238	-4.87	1.18	0.96	12.28	8.05	13.1	169	5.00
FOD1	10.55	201.89	825.53	0.245	3.06	1.15	0.88	13.9	10.2	16.6	325	4.17
FOD2	11.27	201.89	825.53	0.245	2.54	1.20	1.04	12.3	6.20	9.40	132	2.09

4 $C_{n-paraffins}$, concentration of normal paraffins; M , molecular weight; ρ , density; v , molecular volume; T_s ,
5 saturation temperature; $S_{1^\circ C/min}$, supersaturation calculated at 1°C/min; γ , interfacial tension; r_c , critical
6 radius; n , apparent order of nucleation; $\log(k_n)$, base-10 logarithm of the nucleation rate constant; L ,
7 characteristic size of the crystal; G , crystal growth rate.

8

1 **Table 4.** Paraffin dissolution enthalpy (kJ/mol) and entropy (kJ/mol.K) values derived from the
2 van't Hoff Solubility relation, based on experimental dissolution points.

	B0	B7
$\Delta H_{dissolution}$ (kJ/mol)	37.84 ± 6.18	40.56 ± 3.20
$\Delta S_{dissolution}$ (kJ/mol.K)	0.12 ± 0.02	0.14 ± 0.01

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1 **Table 5.** Linear growth rate (G) as a function of cooling rate (β), and the respective kinetic
 2 parameters, k_g and g .

		β ($^{\circ}\text{C}/\text{min}$)				$\ln(k_G)$	g
$S_{1^{\circ}\text{C}/\text{min}}$		0.10	0.17	0.50	1.00		
		G ($\mu\text{m}/\text{s}$)					
B0	1.22	0.44	0.48	0.69	1.24	9.25	2.54
B7	1.26	2.05	2.20	2.54	3.22	7.80	1.90

3

4

1 **Figure 1.** Difference between dissolution and nucleation temperatures for different cooling rates,
2 for the following diesels (experimental error <10%): ♦, B0; ■, B0 2; Δ, B0 4; x, B0 5; □, B0 7; -,
3 B0 8.

4 **Figure 2.** Difference between dissolution and nucleation temperatures for different cooling rates
5 for the following biodiesels (experimental error <10%): ■, B7; Δ, B7 2; x, B7 3; ○, B7 4; □, B7
6 5; ▲, B7 6.

7 **Figure 3.** Solubility curve of a diesel expressed in concentration of normal paraffins higher than
8 11 as a function of dissolution temperature: (■) B0 and (□) B7.

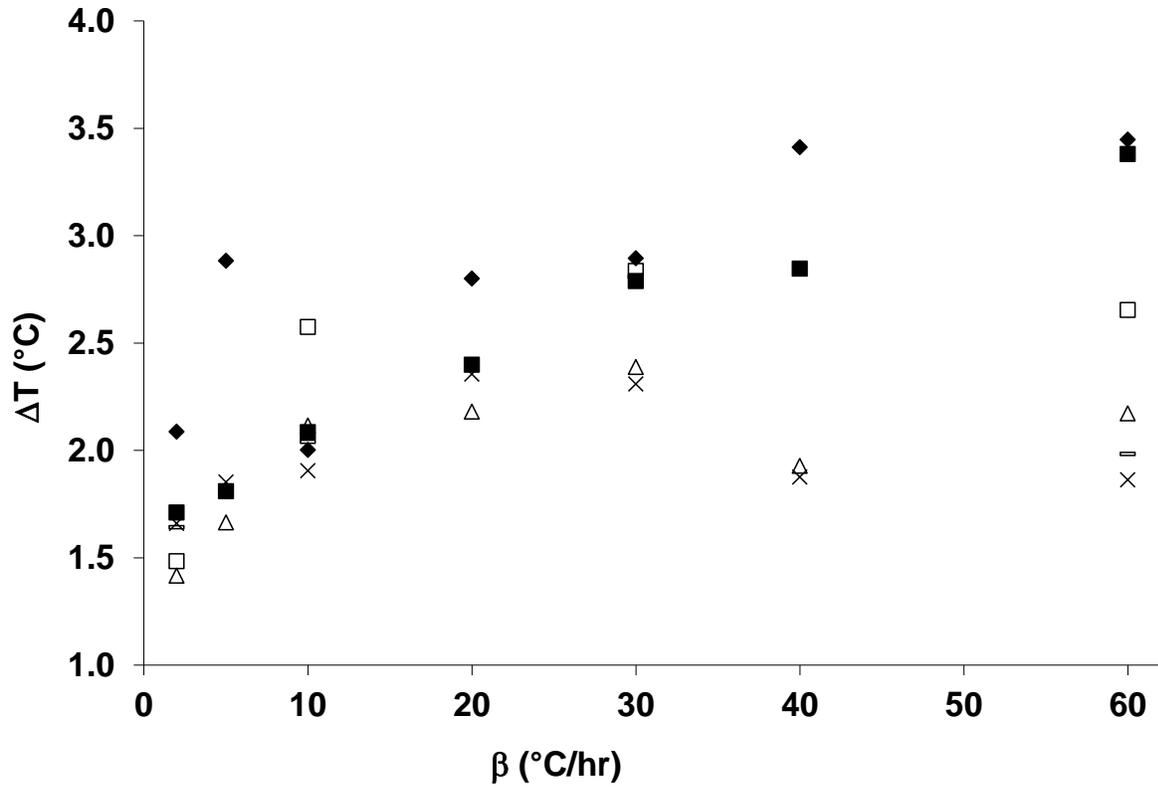
9 **Figure 4.** Effect of supersaturation on the nucleation rate: (a) —, B0, ---, B7, —.—, FOD, (b)
10 mixtures prepared from B0 (—, B0; ■, B0 2; ♦, B0 5; x, B0 8; ●, B0 4) and the corresponding
11 prepared from B7 (—, B7; □, B7 2; ◇, B7 3; *, B7 5; ○, B7 6).

12 **Figure 5.** Images of crystals of different mixtures: a) B0, b) B7, and c) FOD.

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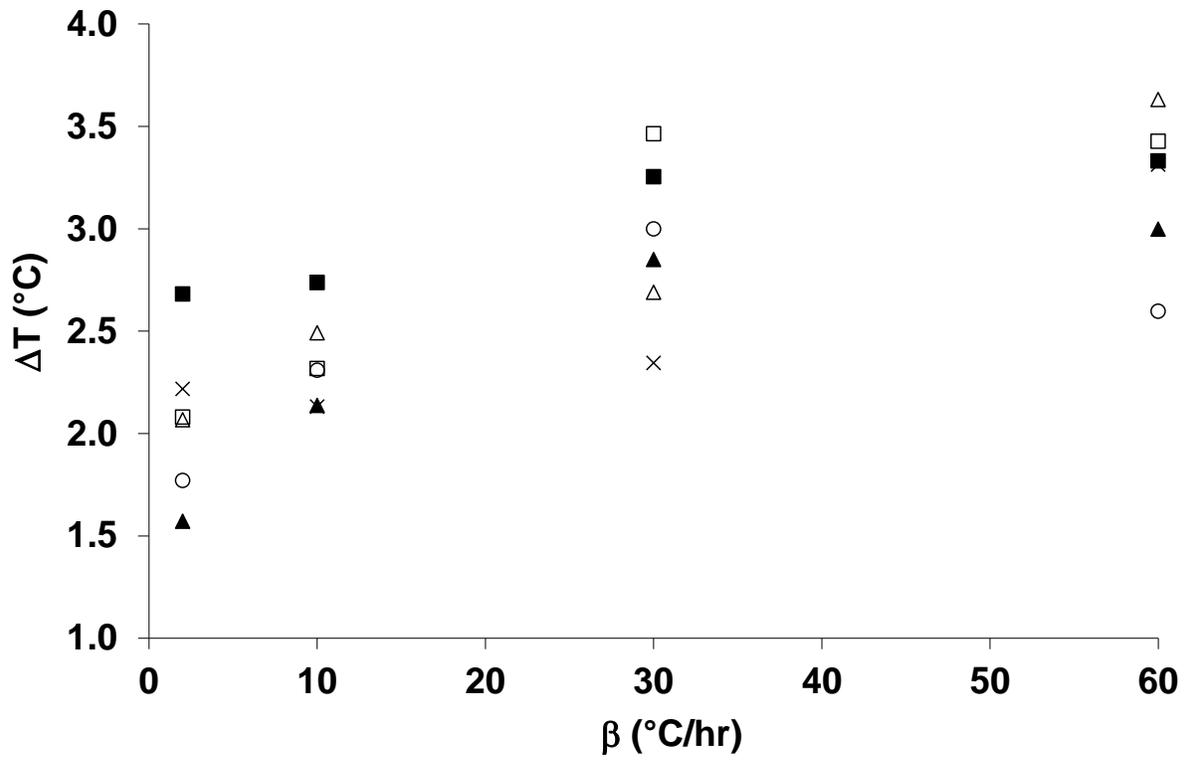
1 **Figure 1**

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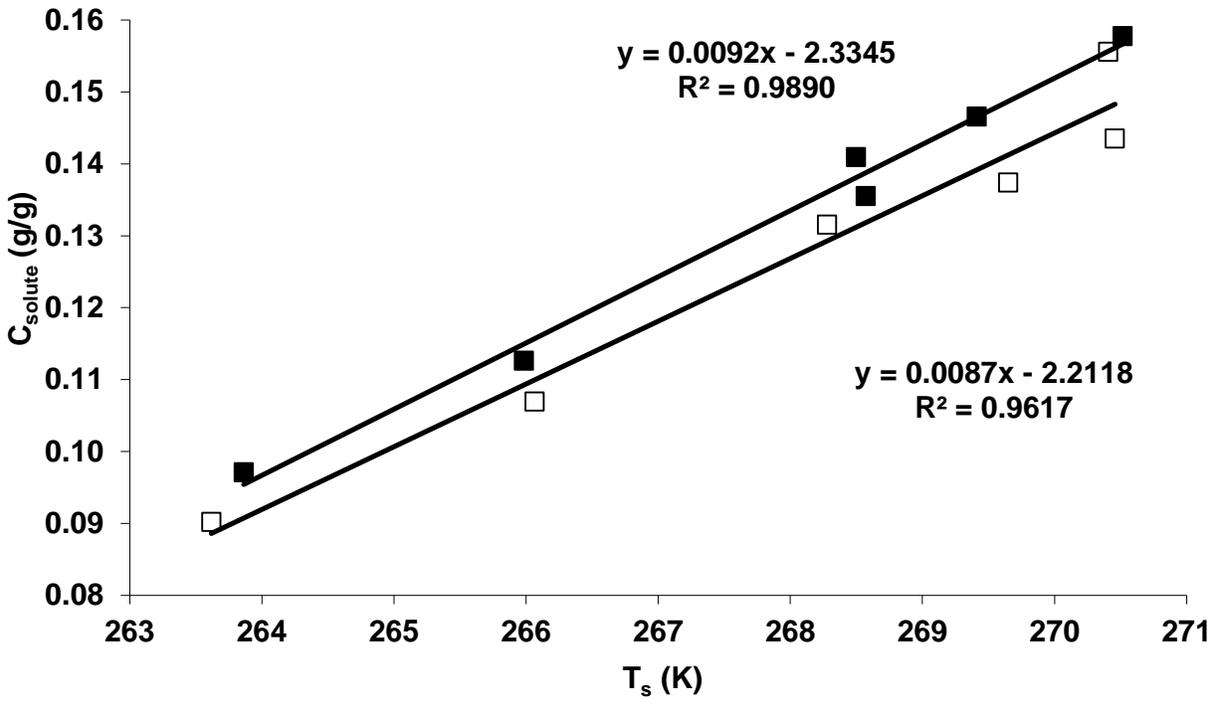
1 Figure 2
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1 **Figure 3**

2



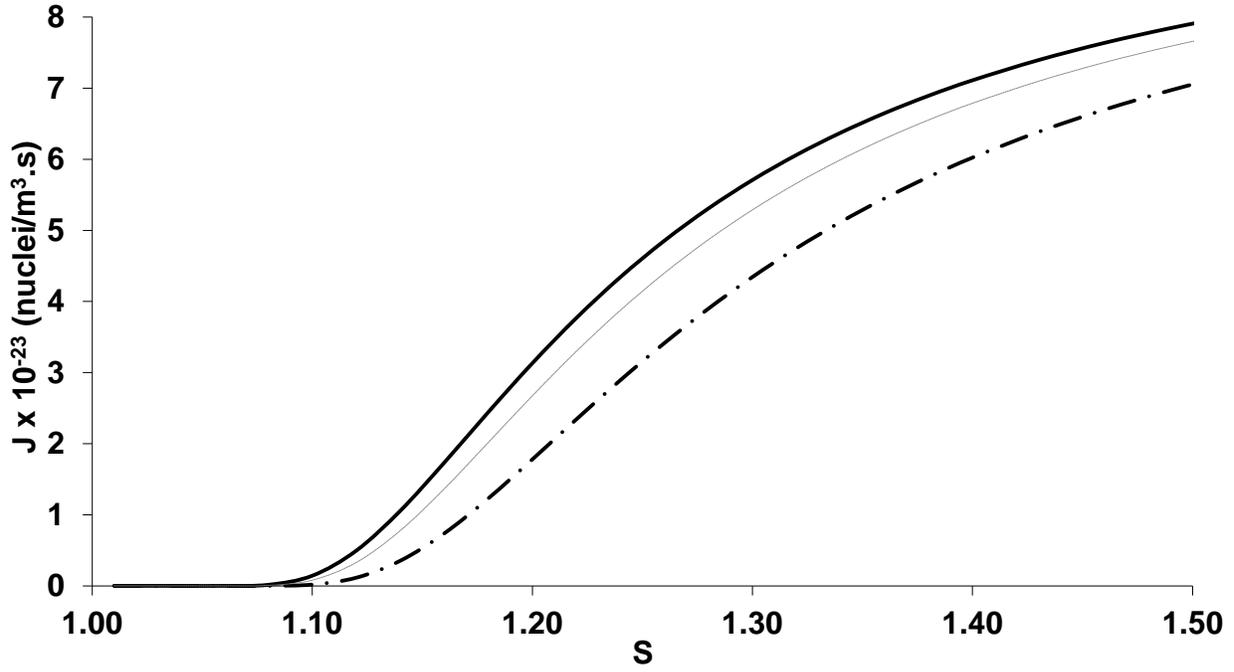
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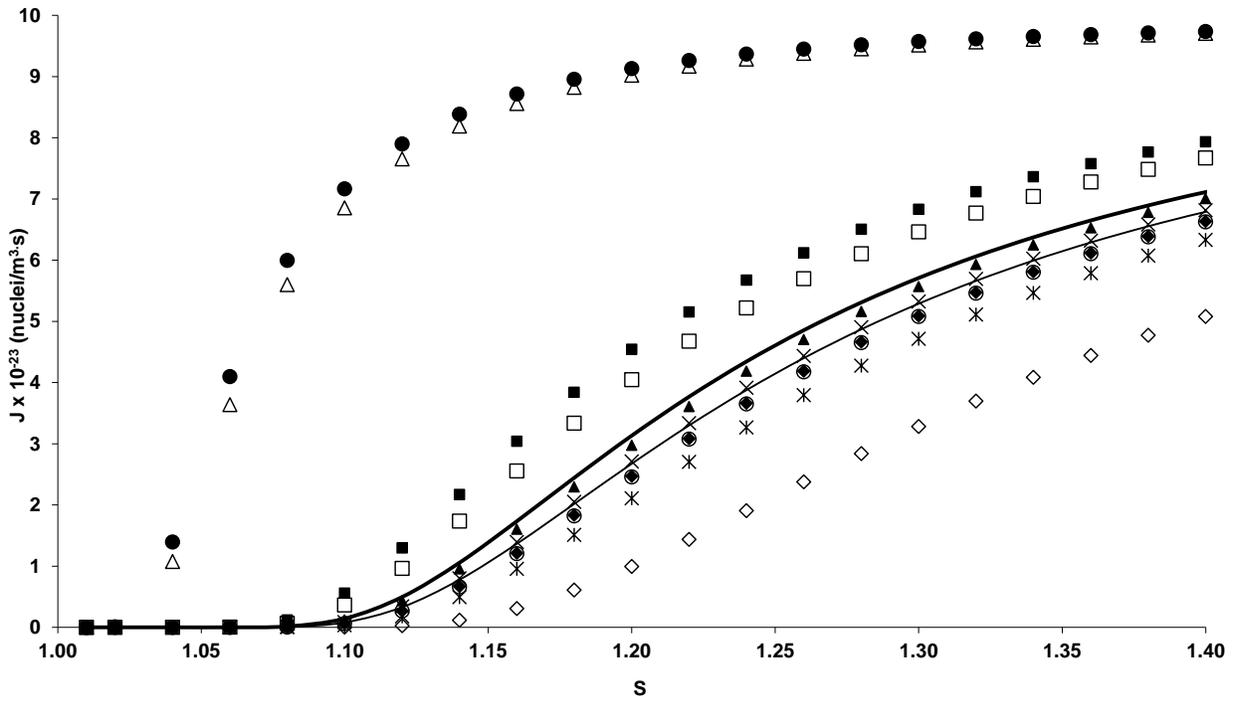
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1 **Figure 4**

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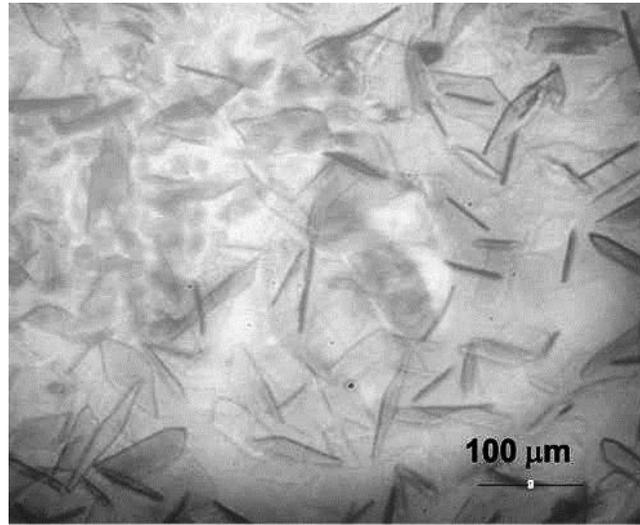
(a)



(b)

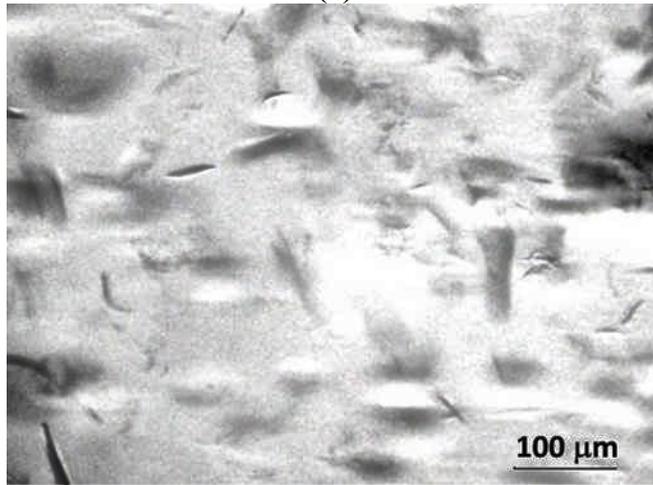
1 **Figure 5**

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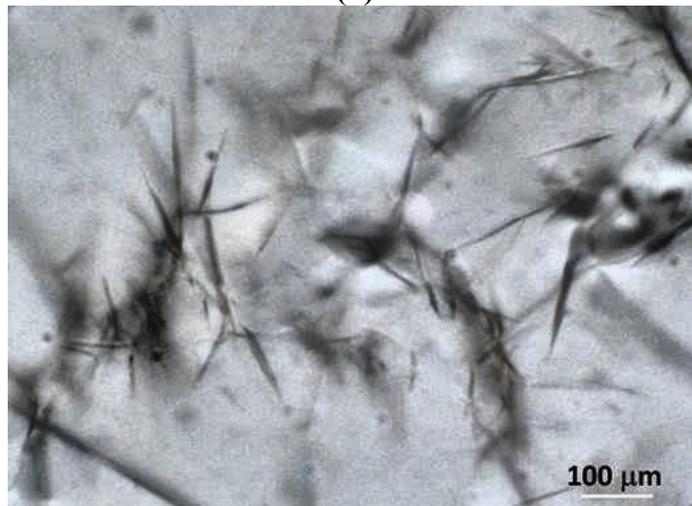
(a)

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(b)

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(c)