

Vegetable Oil Quenchants: Calculation and Comparison of The Cooling Properties of a Series of Vegetable Oils

Nikolai Ivanovich Kobasko¹ - Ester Carvalho de Souza² -
Lauralice de Compos Franceschini Canale^{2,*} - George Edward Totten³
¹ Intensive Quenching Technologies, USA

² Universidade de São Paulo, Escola de Engenharia de São Carlos, Brazil

³ Portland State University, Department of Mechanical and Materials Engineering, USA

The compositions of canola, soybean, corn, cottonseed and sunflower oils suggest that they exhibit substantially different propensity for oxidation following the order of: Canola < corn < cottonseed < sunflower ≈ soybean.

These data suggest that any of the vegetable oils evaluated could be blended with minimal impact on viscosity although compositional differences would surely affect oxidative stability. Cooling curve analysis showed that similar cooling profiles were obtained for different vegetable oils. Interestingly, no film boiling or transition nucleate boiling was observed with any of the vegetable oils and heat transfer occurs only by pure nucleate boiling and convection. High-temperature cooling properties of vegetable oils are considerable faster than those observed for petroleum oil-based quenchants.

©2010 Journal of Mechanical Engineering. All rights reserved.

Keywords: quenchant, heat transfer, vegetable oil, cooling curve, oxidation, cooling curves

0 INTRODUCTION

There have been various investigations on the use of vegetable oils and (animal oils) as quenchants. One of the earliest studies involving cooling curve and heat transfer analysis of quenching properties was conducted by Rose in 1940 with rapeseed oil [1]. The cooling curve results obtained showed that the heat transfer coefficients for rapeseed oil were 1744 to 2092 W/m²K in the transition nucleate boiling region, 2906 to 3486 W/m²K in the nucleate boiling region and 464 to 697 W/m²K in the convective cooling region *versus* 697 to 1394 W/m²K for film boiling, 2325 to 3486 W/m²K nucleate boiling and 233 to 580 W/m²K for convective cooling for a so-called petroleum "heavy oil". The higher cooling rates for rapeseed oil were attributed to the relatively poor stability of the vapor blanket formed by the rapeseed oil [1].

In 1953, Tagaya and Tamura compared the quench severity of different vegetable oils including soybean, rapeseed and castor oils with mineral oils and fish/animal oils with respect to fluid source, viscosity and oxidative stability for various naturally derived fluids [2]. These data showed that although the Grossmann quench severity factors were comparable for both castor oil ($H = 0.199$) and soybean oil ($H = 0.2$), the cooling times from 700 to 300°C were

significantly faster for castor oil (1.8 seconds) than for soybean oil (1.42 seconds) using a JIS K 2242 silver probe test which utilizes a 10 mm dia x 30 mm cylindrical silver probe with a surface thermocouple [3].

Fujimura and Sato followed this work in 1963 by examining the quenching performance of the vegetable oils reported by Tagaya and Tamura and also added castor oil to their study in addition to ethyl esters of oleic, palmitic and stearic acid *versus* different petroleum oil quenchants and concluded that the performance of soybean and rapeseed oil were essentially equivalent [4]. Cooling curve analysis was performed according to JIS K 2242 [3]. Quenching performance of the ethyl esters were also equivalent to each other and exhibited greater quench severity than the vegetable oils. Castor oil, however, was found to be thermally unstable. The quenching performance of castor oil was also studied by Farah, et. al. [5] and the thermal instability of this oil was subsequently confirmed [6].

Currently, the most commonly cited vegetable oil basestocks used for quenchant formulation in the USA are based on canola oil [7] and [8], and soybean oil [9]. Recently, a crambe oil based fluid has been reported as a potential quenchant [10]. Przylecka and Gestwa

*Corr. Author's Address: Universidade de São Paulo, Escola de Engenharia de São Carlos, São Carlos, Brazil, lfcanele@sc.usp.br

have reported the use of a vegetable oil-based quenchant for hardening carburized steels [11]¹.

Prabhu studied the heat flux properties of palm oil [12] and extensive heat transfer and wetting studies of coconut, sunflower, groundnut, palm and castor oils [12] to [15]. With the exception of palm oil, these vegetable oils are not commonly considered as basestocks for quenchants in North and South America. Prabhu's cooling curve analysis work was conducted using a 12 mm dia x 60 mm cylindrical Type 304 stainless steel probe. Interestingly, with the exception of castor oil, relatively little difference in surface wetting properties were obtained and quench severities comparable to a conventional, non-accelerated mineral oil were observed.

Totten et. al. reported the results of cooling curve, hardening performance, heat transfer, and rewettability characterization studies conducted with crude and partially hydrogenated and winterized soybean oils [16] provided by Honary [17]. Because of the strong influence of the test specimen surface on the wetting behavior (and therefore on the quenching behavior), unalloyed (Ck 45) steel probes were used. This work provided a simultaneous examination of the martensitic transformation with local differences, and dependencies on the rewetting time (and dependencies on the metallurgical condition of the steel).

Cooling curve analyses showed that immersion quenching was primarily influenced by the sequence of the cooling phases and different heat transfer rates. Heat transfer on the specimen surface was primarily determined by the rewetting conditions and depended on the cooling characteristics of the quenching medium used, bath temperatures, and agitation rates. The soybean oils investigated showed no significant differences in cooling behavior and rewetting conditions on the test specimen surface and cooling rates were similar. A comparison of the cooling time-temperature and cooling rate curves

showed that vegetable oils exhibited faster cooling rates than the mineral oil used as a reference.

The objective of this study was to compare the quenching performance of vegetable oils most commonly considered as potential basestocks for quenchant formulation in North and South America. Furthermore, for the first time, quenching performance will be considered in conjunction with the compositional variation of the vegetable oils being studied.

1 EXPERIMENTAL

The vegetable oils used for this work were purchased at the local market in Sao Carlos, Brazil and were characterized and used in the as-purchased condition. The vegetable oils that were purchased included: canola oil, cottonseed oil, corn oil, sunflower oil, and soybean oil (commercially designated as "pure" soybean oil). Quenching performance of these oils was compared to two commercially available quenching oils: Micro Temp 157 (a conventional "slow" oil) and Micro Temp 153B (an accelerated "fast" oil).²

Viscosity was measured at 40 and 100°C according to: ASTM D445 - 06 Standard Test. The viscosity index was determined from the kinematic viscosities at 40 and 100°C according to ASTM D2270 - 04.

The fatty acid ester composition of the vegetable oil was determined by a gas chromatographic analysis procedure using methyl ester derivatives of the different vegetable oils prepared as described previously [18] and [19] using a Model CG-17-A Shimadzu gas chromatograph equipped with a flame ionization detector (FID) set to 300°C and a "split" injection system ratio of 1:30 at 280°C. An injection volume of 1 µL was used. N₂ was used as an auxiliary gas and average linear H₂ gas flow rate was 35 cm/s. The column used was LM-100 (100% polyethylene glycol) with dimensions 25m x 0.25 mm i.d. x 0.25 µm. The temperature of the

¹ The specific product reported by Prezylecka and Gestwa was a commercial product designated as Bioquench 700 manufactured by Houghton International. In the USA, this product is based on canola oil (see References 17 and 56). However, in Poland, this product was reportedly based on rapeseed oil.

² The Micro Temp 157 and Micro Temp 153B were obtained from Micro Quimica Ind. Com. Ltda., Rua Projetada 225, Jardim União, 09970-000 Diadema - SP, Brazil: www.micro-quimica.ind.br

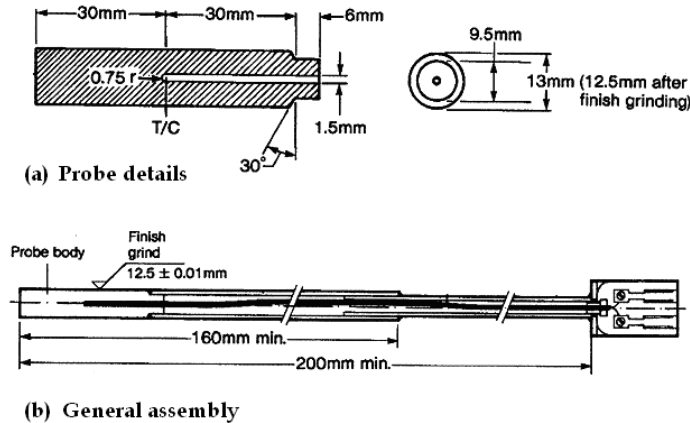


Fig. 1. Schematic illustration of the probe used for cooling curve analysis in ASTM D6200

column was maintained isothermally at 190°C for 25 minutes.

The cooling curves were obtained in the non-agitated condition at 60°C according to ASTM D6200 which utilizes a 12.5 mm dia x 60 mm INCONEL 600 cylindrical probe with a Type K thermocouple inserted to the geometric center. After heating the probe in a furnace to 850°C, it was then manually and rapidly immersed into 2000 mL of the oil to be tested which was contained in a tall-form stainless steel beaker. The probe temperature and cooling times are recorded at selected time intervals to establish a cooling temperature versus time curve. From these curves the critical parameters are obtained, as illustrated in Fig. 2 [20], for quenchant characterization [21].

- I t_{A-B} [sec],
- II T_{A-B} [°C],
- III D_{Hmin} [°C/sec],
- IV C_{R700} [°C/sec],
- V C_{Rmax} [°C/sec],
- VI T_{CRmax} [°C],
- VII I C_{R300} [°C/sec],
- VIII C_{R200} [°C/sec],
- IX t_{300} [sec]
- X t_{200} [sec]

Parameters I to III shown graphically in Fig. 2 are related to the full-film boiling (vapor blanket cooling) to nucleate boiling transition time and temperature and the cooling rate at critical temperatures. Cooling rate at 700°C, parameter IV, is measured since it is usually desirable to maximize this cooling rate to avoid the steel pearlite transformation region. Parameters V and VI are the maximum rate of

cooling and the temperature where this occurs. Generally, it would be desirable to maximize CR_{max} and minimize TCR_{max} . The rates of cooling at temperatures such as 200 and 300°C, parameters VII and IX, are also determined since they are related to the potential for steel cracking and distortion. To minimize these problems, it is desirable to minimize cooling rates in this region. Parameters VIII and X are related to region of the pearlite transformation. It is generally desirable to minimize these parameters.

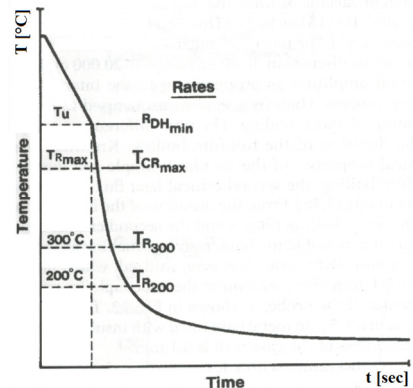


Fig. 2. Critical cooling curve parameters

1.1 Calculation of Effective Heat Transfer Coefficients

Most conventional cooling processes involving vaporizable quenchants possess four cooling mechanisms: 1) shock boiling, 2) film boiling, 3) nucleate boiling and 4) convection cooling processes. Since standard probe provides

cooling rate and temperature vs. time at the core of probe, we can only evaluate average effective heat transfer coefficients which are widely used in heat treating industry. During quenching, the heat transfer coefficient is dependent on: surface temperature of the steel part, mass and flow velocity of the quenchant. The variation of the heat transfer coefficient during film boiling is sufficiently small to permit the use of average values (α_{FB}). During nucleate boiling and convections also average effective heat transfer coefficients can be found. In this paper the heat transfer coefficients were calculated according to the theory of regular conditions. [22] to [24]. The calculation procedure has been discussed previously in References [15] and [25] and is outlined below.

The equation governing heat conduction for one dimensional heat transfer, as would be expected from the 12.5 mm dia x 60 mm cylindrical standard probe illustrated in Fig. 1, is:

$$\frac{1}{a} \frac{\partial T}{\partial t} = \text{div}(\text{grad } T) \quad (1)$$

where T [K] is temperature at the center of the probe, t is time [s], a [m^2/s] is the thermal diffusivity of the metal.

The boundary and initial conditions are:

$$\frac{\partial T}{\partial r} + \frac{\alpha}{\lambda} (T - T_m) \Big|_{r=R} = 0 \quad (2)$$

$$T(r,0) = T_0 \quad (3)$$

$$\frac{\partial T}{\partial r} = 0 \quad (4)$$

where λ [W/mK] is the heat conductivity of the metal, α [W/m²K] is the heat transfer coefficient, T [K] is the temperature at the center of the probe, T_m [K] is the medium temperature, R [m] is radius. The general solution for these equations is:

$$\frac{T - T_m}{T_0 - T_m} = \sum_{i=0}^{\infty} A_i U_i \exp(-m_i t) \quad (5)$$

where: $m_0 < m_1 < m_2 < \dots$ (6)

where: A_i is temperature amplitudes, U_i is the functions of the coordinates, m_i [s^{-1}] is a value that depends on the thermal properties of a material and cooling capacity of the quenchant, t [s] is cooling time.

In regular condition Eq. (5) can be rewritten as:

$$\frac{T - T_m}{T_0 - T_m} = A_0 U_0 \exp(-mt). \quad (7)$$

The value "m" from Eq. (7) is measured by using two points on the temperature-time curve (cooling curve) that correspond to time t_1 and time t_2 i.e.:

$$\ln\left(\frac{T_1 - T_m}{T_0 - T_m}\right) = \ln(A_0 U_0) - mt_1, \quad (8)$$

$$\ln\left(\frac{T_2 - T_m}{T_0 - T_m}\right) = \ln(A_0 U_0) - mt_2,$$

or:

$$m = \frac{\ln(T_1 - T_m) - \ln(T_2 - T_m)}{t_2 - t_1}. \quad (9)$$

Using the value of m , the Kondratjev number (Kn) is calculated from:

$$Kn = \frac{m}{m\alpha}, \quad m\alpha = \frac{a}{K}, \quad (10)$$

where K is the Kondratjev form factor (shape factor). For a cylinder, K is:

$$K = \frac{R^2}{5.783}. \quad (11)$$

Since the standard probe shown in Fig. 1 is used to obtain temperature-time and cooling rate - time data for the cooling process, then Eq. (5) is rewritten as:

$$w = m(T - T_m) \quad (12)$$

$$\text{or } m = \frac{w}{T - T_m}. \quad (13)$$

where w is the cooling rate. Eq. (9) or Eq. (13) may be used to determine the Kondratjev number Kn from Eq. (10).

The generalized Biot number and further average effective heat transfer coefficient during quenching are evaluated from the universal correlation (14):

$$Kn = \frac{Bi_v}{(Bi_v^2 + 1.437 Bi_v + 1)^{0.5}}. \quad (14)$$

Assume that generalized Biot number from the experiment is equal to value C , i.e.

$$Bi_v = C$$

$$\text{where: } Bi_v = \frac{\alpha}{\lambda} K \frac{S}{V} \quad (15)$$

where: S is the surface area of the probe, V is the volume of the probe, K is Kondratjev form factor.

The heat transfer coefficient can be evaluated as:

$$\alpha = \frac{C\lambda V}{KS} = \frac{C\lambda R}{2K} \quad (16)$$

Two examples are provided which illustrate the use of these equations.

Example 1

Assume that the core cooling rate of the standard probe when quenching in oil (60°C) at 700°C is 90°C/s. Thermal diffusivity of Inconel 600 at 700°C is equal to $5.6 \cdot 10^{-6} \text{ m}^2/\text{s}$ and the thermal conductivity is equal to 25.9 W/mK. The average heat transfer coefficient at this temperature can be calculated using Eq. (16). First, the value of m is calculated from Eq. (13), i.e.

$$m = \frac{90^\circ \text{C}/\text{s}}{700^\circ \text{C} - 60^\circ \text{C}} = 0.14 \text{ s}^{-1}.$$

Then calculate:

$$m_\infty = \frac{a}{K} = \frac{5.6 \cdot 10^{-6} \text{ m}^2/\text{s}}{6.75 \cdot 10^{-6} \text{ m}^2} = 0.83 \text{ s}^{-1},$$

According to Eq. (10), the Kondratjev number $Kn = 0.14/0.83 = 0.189$. From the correlation (14) it follows that the generalized Biot number $Bi_V = 0.19$. Using Eq. (16), the average heat transfer coefficient is calculated from:

$$\alpha = \frac{0.19 \cdot 25.9 \text{ W/mK} \cdot 6.25 \text{ m} \cdot 10^{-3}}{2 \cdot 6.75 \cdot 10^{-6} \text{ m}^2} = 2278 \frac{\text{W}}{\text{m}^2 \text{K}}$$

Example 2

Assume that the core cooling rate of the standard probe when quenching in oil (60°C) at 450°C is 50°C/s. Thermal diffusivity of Inconel 600 at 450°C is equal to $4.9 \cdot 10^{-6} \text{ m}^2/\text{s}$ and heat conductivity is equal to 20.7 W/mK. There is need to calculate average heat transfer coefficient using Eq. (16). As with Example 1, the value of m is calculated using Eq. (13):

$$m = \frac{50^\circ \text{C}/\text{s}}{450^\circ \text{C} - 60^\circ \text{C}} = 0.128 \text{ s}^{-1}.$$

Then the value of m_∞ is calculated:

$$m_\infty = \frac{a}{K} = \frac{4.9 \cdot 10^{-6} \text{ m}^2/\text{s}}{6.75 \cdot 10^{-6} \text{ m}^2} = 0.726 \text{ s}^{-1},$$

where for standard probe $K = 6.75 \cdot 10^{-6} \text{ m}^2$.

According to Eq. (10) Kondratjev number $Kn = 0.128/0.726 = 0.176$. From the correlation (14) follows that generalized Biot number $Bi_V = 0.20$. Using Eq. (16), the average heat transfer coefficient is:

$$\alpha = \frac{0.20 \cdot 20.7 \text{ W/mK} \cdot 6.25 \text{ m} \cdot 10^{-3}}{2 \cdot 6.75 \cdot 10^{-6} \text{ m}^2} = 1916 \frac{\text{W}}{\text{m}^2 \text{K}}.$$

The average effective heat transfer coefficient within the temperature range 450 to 700°C is equal to:

$$\alpha = \frac{2278 + 1916}{2} = 2097 \frac{\text{W}}{\text{m}^2 \text{K}}.$$

3 RESULTS AND DISCUSSION

3.1 Compositional Analysis

The composition of the different vegetable oils used for the work reported here was determined by methanolysis of the vegetable oil. The components were quantified by gas chromatographic analysis and the results obtained are shown in Table 1. Substantial variation in the compositions of these vegetable oils is evident.

The stability of vegetable oils to oxidation depends not only on the degree of unsaturation (double bond content) but also on the degree of double bond conjugation. For example, linoleic acid is especially reactive relative to oleic acid and linolenic acid is more reactive than linoleic acid. The most stable form of the fatty acid components is when there are no double bonds present (completely saturated) such as stearic acid and palmitic acid. Schneider has reported that the relative rate of oxidation increases as the number of double bonds in conjugation with each other [26]. The following approximate relative oxidation rates were reported: stearic (1) > oleic (10) > linoleic (100) > linolenic (200). Similar results have been reported by Kodali [27]. For this work, it is assumed that the relative rate of oxidation of stearic acid is approximately equivalent to palmitic acid which is reasonable since both are saturated (no hydrocarbon double bonds) with very similar molecular weights.

It is also known that the overall reaction rate of a process is the sum of the various

Table 1. *Composition percentage of fatty acids present in samples of vegetable oils¹*

Vegetable Oil	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acid	Relative Reactivity to Oxidative Degradation ²
Corn	12.0	2.0	35.0	48.0	0.8	1.43
Soybean	10.5	2.7	20.8	58.6	5.0	1.90
Canola	4.5	2.1	65.4	20.2	5.2	1
Cottonseed	22.0	2.0	17.0	56.7	0.4	1.60
Sunflower	7.0	3.2	19.4	66.0	0.5	1.85

1. Percentages may not add up to 100% due to presence of other minor constituents not listed.
2. Calculated from the stearic acid, oleic acid, linoleic acid and linolenic acids using the reported relative reactivity to oxidation of: 1/10/100/200 respectively.

individual reaction rates of a process. Since vegetable oils possess different fatty acid components, each with a particular and different oxidation rate, the overall oxidation rate is approximately equivalent to the sum of the oxidation rates of the fractional composition of stearic (and palmitic), oleic, linoleic and linolenic acids. This is only approximate since there are other unidentified unsaturated fatty acid components in very low concentrations. This is the reason why different vegetable oils exhibit different inherent properties such as smoke and flash points, for example or why one vegetable oil may be favored for an application, such as deep frying, relative to another.

An approximation of the relative propensity for oxidation of the different vegetable oils with respect to their composition was determined from the fatty acid composition data obtained by gas chromatography and the relative reactivity for oxidation reported by Kodali [27]. The first step in this assessment is to determine the molar quantities of each component in a given quantity of the vegetable oil. The molar quantities of each component are then multiplied by the relative reactivity for oxidation. These component oxidation propensities are summed and normalized to provide a total potential for oxidation ratio of each oil shown in Table 1. These data show that soybean oil would exhibit one of the worst potentials for oxidative instability and canola oil would be the best of those vegetable oils shown here. Based on the compositions of the vegetable oils with respect to stearic acid, oleic acid, linoleic acid and linolenic acid and the relative oxidation rates of: 1/10/100/200 respectively, the data in Table 1 show that the

particular vegetable oils being evaluated would exhibit the relative stability to oxidation of:

$$\text{anola} > \text{corn} > \text{cottonseed} > \text{sunflower} \approx \text{soybean}.$$

Interestingly, while soybean oil is one of the vegetable oils of greatest interest for quenchant formulation, it is almost twice the potential for oxidation than canola oil, the most stable oil in this study.

2.2 Kinematic Viscosity Properties

In addition to oxidative stability, perhaps the most important physical property of any potential quenchant, including vegetable oils, is the viscosity – temperature relationship since it is perhaps the single greatest factor impacting overall heat transfer performance during quenching. For vegetable oils, viscosity typically increases with fatty acid ester chain length and decreases with the amount of unsaturation in the fatty acid ester alkyl chain [28]. Fasina, et. al. studied the viscosity-temperature behavior of 12 vegetable oils and found them all to exhibit an exponential viscosity increase with decreasing temperature [29]. In this work, the viscosity-temperature properties were determined from kinematic viscosity measurements (ASTM D445) and calculation of the viscosity index (VI) according to ASTM D2270 and the data obtained for both the vegetable oils and the two petroleum oil quenchants also being studied are shown in Table 2.

The heat transfer properties of a quenchant is exponentially dependent on fluid viscosity. The viscosities of the different vegetable oils used in this study were

determined and while they are somewhat different from each other, they are comparable and reasonably similar to the two petroleum oil quenchants used for comparative evaluation in this work and included a conventional quench oil (Micro Temp 157) and an accelerated quench oil (Micro Temp 153B).

The rate at which the viscosity of an oil will change as the temperature is increased or decreased is defined as the viscosity index (VI) and determined by measuring the viscosities of an oil at 40 and 100°C and using the tables or equations provided in ASTM D2270. The sensitivity of the change in viscosity with respect to temperature decreases as the VI value increases. In all cases, the VI values shown for the vegetable oils in Table 2 were approximately double those values obtained for the petroleum oil quenchants. Which means that the viscosity of the petroleum oil is much more sensitive to variations in temperature than any of the vegetable oils used in this study. (Both of the petroleum oil quenchants used in this study were formulated from a paraffinic basestock and the higher viscosity exhibited by Micro Temp 153B relative to Micro Temp 157 is due to the presence of cooling rate accelerating additive(s) in the quench oil.)

2.3 Quenching Performance

Quenching performance of each of the vegetable oils was evaluated by cooling curve analysis according to ASTM D6200 which is conducted under unagitated conditions. Since the objective is to use a vegetable oil as a replacement for a petroleum oil, two different petroleum oil quenchants were used for

comparison; Micro Temp 157, a conventional, unaccelerated petroleum oil, and Micro Temp 153B, an accelerated petroleum oil.

During the course of these investigations, it was readily apparent that vegetable oils do not boil under atmospheric conditions and the interfacial temperatures encountered during quenching. This is important because there is no full-film boiling or nucleate boiling involved. Although vegetable-oil based quenchants have been reported before, the fact that they only exhibit convective heat transfer and no full-film boiling or nucleate boiling is not well-known. This performance should be compared to petroleum derived quenchants since, as a class, since they do exhibit full-film boiling and nucleate boiling in addition to convective heat transfer. These differences are apparent when viewing the cooling curves obtained for the vegetable oils in this study with the conventional oil Microtemp 157 and accelerated quench oil, Microtemp 153B shown in Fig. 3.

Petroleum oil quenchants are also often typified by exhibiting relatively little difference in cooling behavior with temperature change. This is usually explained by the smaller difference in ΔT between the metal surface and the bulk temperature of the oil which is approximately counterbalanced by the lower fluid viscosity at the higher bulk fluid temperature.

The data in Table 3 shows that the maximum cooling rate C_{Rmax} and the temperature where this occurs TC_{Rmax} does not vary significantly between different vegetable oils. This conclusion is based on the reported Precision and Bias for ASTM D6200 where the

Table 2. Summary of viscosity properties determined for vegetable oils and petroleum oil based quenchants used in this work.

Viscosity and Viscosity Index	Vegetable Oil					Petroleum Oil Quenchant	
	Canola	Corn	Cottonseed	Soybean	Sunflower	Slow	Fast
						Micro	
						157	153 B
Viscosity (cSt at 40°C)	34.92	33.51	33.86	31.49	33.21	29.0	40.0
Viscosity (cSt at 100°C)	7.91	7.70	7.75	7.51	7.78	5.0	6.65
Viscosity Index	209	211	211	220	218	96	121

maximum cooling rate variation obtained for a reference oil in a round-robin study was 47 to 53°C/s and the temperature at the maximum cooling rate varied in this study between 490 to 530°C.

Overall, the cooling properties of the vegetable oils were comparable to each other and it is notable that only convective cooling was obtained with no extended vapor blanket cooling (film-boiling). This cooling profile shows that vegetable oils would not require a cooling rate accelerator and would be acceptable even for difficult to harden, crack-sensitive carbon steels. The cooling rates, however, were somewhat faster, especially in the critical martensitic temperature transition range (300°C) than the petroleum oil quenchants evaluated suggesting that they may not be as desirable for higher alloy, crack sensitive steels. However, this must be confirmed experimentally.

The Micro Temp 157 and 153B did behave as expected. The fast oil, Micro Temp 153B exhibited shorter film-boiling times and both oils exhibited similar lower temperature cooling rates, although the Micro Temp 153B was somewhat slower which was probably due to the higher bulk fluid viscosity.

The comparison of the heat transfer coefficients and Grossman quench severity values for the vegetable oils evaluated also shows that all of the vegetable oils exhibited comparable heat transfer performance in the hardening temperature range of 700 to 450°C. Interestingly, both the unaccelerated and accelerated petroleum oils evaluated exhibited substantially lower heat

transfer at 700°C than those obtained for the vegetable oils but the heat transfer properties were comparable at the lower temperature of 450°C. On average, the heat transfer coefficients were somewhat lower for the petroleum oil-based quenchants as were the Grossman quench severity values confirming that they exhibit lower quench severity than would be expected for a vegetable oil.

In his study of vegetable oil quenchants Rose observed that the cooling process was very fast initially but it was not recognized that the cooling occurred by convection without film boiling or nucleate boiling [1]. Tamura studied different vegetable and animal oils (triglycerides) and showed that the quench severity was somewhat greater for triglycerides in general than for petroleum oil quenchants. For example, Tamura obtained Grossman H-values of 0.2, 0.199, 0.2 and 0.199 for soybean, fin whate, sperm skin and rapeseed oils respectively and 0.142 and 0.136 for conventional petroleum oils designated as "A" and "B" respectively [2]. Prabhu, et. al. studied the quenching properties of a number of vegetable oils including: sunflower, coconut, palm, and groundnut (peanut) oils and compared the quench severities obtained with a petroleum oil. They reported that the quench severities of these oils followed a decreasing order [15]:

Sunflower oil > Coconut oil > Palm oil >
Petroleum oil > Groundnut oil.

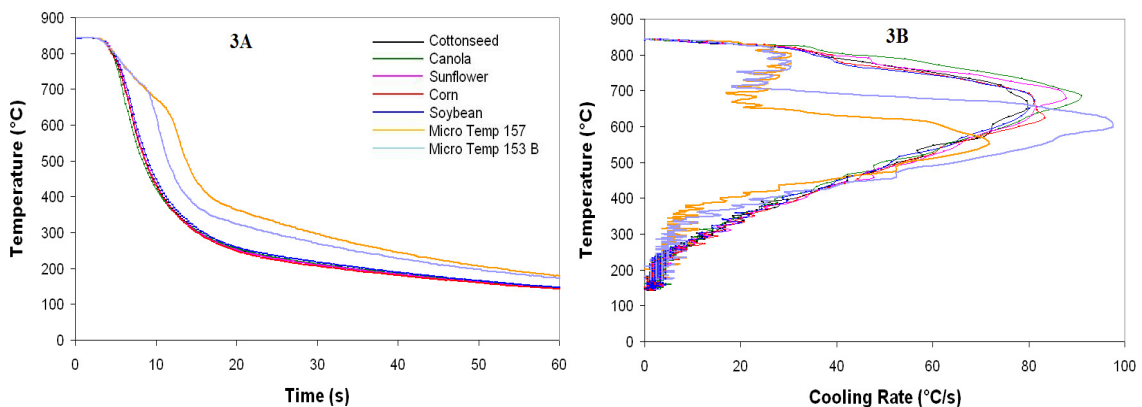


Fig. 3. Cooling curves data at 60°C bath temperature. a) time - temperature, b) cooling rate - temperature

Table 3. Tabulation of cooling parameters obtained by ASTM D6200 at a quench bath temperature of 60°C and with no agitation

Cooling Parameters at 60°C	Vegetable Oil					Petroleum Oil Quenchant	
						Slow Oil	Fast Oil
	Canola	Corn	Cottonseed	Soybean	Sunflower	Micro Temp 157	Micro Temp 153 B
t_{A-B} [s]	3.8	3.3	3.3	3.8	3.8	11.0	8.5
T_{A-B} [°C]	830.0	837.7	835.0	826.5	830	652.3	703.4
$CR_{DH \min}$ [°C/s]	19.4	14.6	20.0	20.6	16.3	20.7	29.2
C_{Rmax} [°C/s]	90.9	81.7	79.5	81.2	87.6	71.7	97.3
TC_{Rmax} [°C]	686.0	668.4	648.9	673.6	677.2	550.8	598.8
C_{R700} [°C/s]	86.0	77.0	75.0	75.0	86.0	25.0	29.0
C_{R300} [°C/s]	11.4	12.4	14.0	11.4	11.4	4.9	6.0
C_{R200} [°C/s]	2.7	2.7	2.1	2.7	2.2	2.4	1.2
$t_{300°C}$ [s]	15.3	15.0	15.5	15.8	15.3	29.3	24.0
$t_{200°C}$ [s]	34.0	32.3	34.0	35.8	33.5	52.0	48.8

Heat transfer properties

Heat transfer coefficient [W/m ² K) at 700 °C	2455	2160	2190	2040	2455	587	705
Heat transfer coefficient [W/m ² K) at 450 °C	1810	1815	1970	1810	1980	1790	2060
Average value [W/m ² K)	2132	1842	2080	1920	2212	1188	1382
Grossman H-value	0.198	0.171	0.193	0.178	0.205	0.111	0.124

With the exception of groundnut oil, the other vegetable oils shown here exhibited greater quench severities than the petroleum oil reference evaluated. The relatively low quench severity of groundnut oil compared to the other oils shown was at least partially attributable to low activation energies for spreading (poor wetting) [12].

Although the series of vegetable oils used for this work are different than those of other studies reported earlier, the quenching properties are consistent with those reported earlier. In fact, the Grossmann quench severities

were nearly identical to those reported by Tamura.

4 CONCLUSIONS

Five vegetable oils were obtained from a commercial source and their compositions were determined by gas chromatography. Based on the compositions of the vegetable oils with respect to stearic acid, oleic acid, linoleic acid and linolenic acid the particular vegetable oils being evaluated would exhibit the relative stability to oxidation of:

Canola < corn < cottonseed < sunflower ≈
soybean.

Interestingly, while soybean oil is one of the vegetable oils of greatest interest for quenchant formulation, it has almost twice the potential for oxidation than canola oil, the most stable oil in this study. It is recognized that this can only provide a rough estimate of vegetable oil stability since other factors not included in this simplified computation also affect oxidative stability of vegetable oils such as: peroxide content, presence of free acids and water, metal contamination and other affects. Nevertheless, this calculation does show the dependence of the oxidative stability of vegetable oils on compositional structure and furthermore, these results are comparable to results using pressurized differential scanning calorimetry [30].

Viscosities at 40 and 100°C by ASTM D445 and the viscosity index by ASTM D2270 were determined for the vegetable oils and two petroleum oil quenchants: Microtemp 157 [a conventional slow oil) and Microtemp 153B (an accelerated or fast oil). Although the kinematic viscosities of different vegetable and petroleum oils at 40°C were not identical, they were similar. However, the VI values for different vegetable oils were very close and varied between 209 to 220 and were all much higher than the VI values obtained for Microtemp 157 [96) and Microtemp 153B [121). These data indicate that the viscosity variation of these vegetable oils are substantially less sensitive to temperature variation than the paraffinic oil based Microtemp 157 and Microtemp 153B. Although these data suggest that any of the vegetable oils evaluated could be blended with minimal impact on viscosity, the oxidative stability would surely be substantially impacted.

Cooling curve analysis was performed on these vegetable oils at 60°C under non-agitated conditions according to ASTM D6200. These results were compared with cooling curves obtained for Microtemp 157, a conventional, unaccelerated petroleum oil, and Microtemp 153B, an accelerated petroleum oil under the same conditions. The results showed that the high-temperature cooling profiles were very similar for the different vegetable oils and at lower probe temperatures and a somewhat greater discrimination of the cooling properties

of the different vegetable oils was observed. When the cooling curve data of the different vegetable oils is compared to the petroleum derived Microtemp 157 and Microtemp 153B, it is evident that all of the vegetable oils do not exhibit film boiling or transition nucleate boiling. In fact, although Microtemp 153B, the accelerated quench oil exhibited significantly reduced film-boiling stability relative to Microtemp 157, the conventional quench oil, it's high-temperature cooling performance was not as "fast" as the vegetable oils. These data are reasonable since vegetable oils do not boil due to their extraordinarily high boiling point. Instead, they would degrade before boiling under atmospheric conditions. The cooling properties obtained suggest that vegetable oils would be especially suitable for quenching low-hardenability steels such as carbon steels.

5 ACKNOWLEDGEMENTS

The authors acknowledge their appreciation to CAPES [Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the financial support of this work and to MSc Renata Leal for performing the physical property analysis reported here.

6 REFERENCES

- [1] Rose, A. (1940) The cooling capacity of the quenchants, *Archiv. für das Eisenhüttenwesen*, vol. 13, no. 8, p. 345-354.
- [2] Tagaya, M., Tamura, I. (1954) Studies on the quenching media 3rd report, The cooling ability of oils, *Technology Report, Osaka University*, vol. 4, p. 305-319.
- [3] JIS K 2242:1980, *Japanese Industrial Standard – Heat Treating Oil*.
- [4] Fujimura, Y., Sato, T. (1963) The composition of quenching oil and quenching effects, *The Iron and Steel Institute of Japan (ISIJ)*, vol. 49, p. 1008-1015.
- [5] Farah, A.F., Crnkovic, O.R., Canale, L.C.F. (1999) Castor oil: Studies for heat treatment applications, 19th *Heat Treating Society Conference Proceedings*, ASM International, Materials Park, OH, p. 251-254.

- [6] Canale, L.C.F., Fernandes, M.R., Agostinho, S.C.M., Totten, G.E., Farah, A.F. (2005) Oxidation of vegetable oils and its impact on quenching performance, *Int. J. Materials and Product Technology*, vol. 24, no. 1-4, p. 101-125.
- [7] Brennan, R.J., Faulkner, C.H., Massuda, D. (1997) A quenchant based on canola oil, *Advanced Materials & Processes*, vol. 152, no. 2, p. 32S – 32U.
- [8] Brennan, R.J., Faulkner, C.H. (1996) A new quenching alternative, *Conf. Proceed. 2nd International Conference on Quenching and Control of Distortion.*, ASM International, Materials, p. 423-428.
- [9] Honary, L.A.T. (1996) Performance of vegetable oils as a heat treat quenchant, *Conf. Proceed. 2nd International Conference on Quenching and Control of Distortion*, ASM International, Materials OH, p. 595-605.
- [10] Lazerri, L., De Mattei, F. Bucelli, F., Palmieri, S. (1999) Crambe oil: A potentially new hydraulic oil and quenchant, *Ind. Lubr. Tribol.*, vol. 49, no. 2, p. 71-77.
- [11] Przylecka, M., Gestwa, W. (2007) The influence of Bio-Quench 700EU: Conditions on hardness of carburized components, *Inżynieria Materialowa*, vol. XXVIII, no. 3-4, p. 715-719.
- [12] Prabhu, K.N., Fernandes, P. (2007) Determination of wetting behavior, spread activation energy, and quench severity of bioquenchants, *Metallurgical and Materials Transactions B*, vol. 38, no. 4, p. 631-640.
- [13] Prabhu, K.N., Prasad, A. (2003) Metal/quenchant interfacial heat flux transients during quenching in conventional quench media and vegetable oils, *J. Mat. Eng. and Perf.*, v. 12, no. 1, p. 48-55.
- [14] Prabhu, K.N., Fernandes, P. (2007) Effect of surface roughness on metal/quenchant interfacial heat transfer and evolution of microstructure, *Materials and Design*, vol. 28, p. 544-550.
- [15] Fernandes, P., Prabhu, K.N. (2008) Comparative study of heat transfer and wetting behaviour of conventional and bioquenchants for industrial heat treatment, *International Journal of Heat and Mass Transfer*, vol. 51, no. 3-4, p. 526-538.
- [16] Totten, G.E., Tensi, H.M., Lanier, K. (1999) Performance of vegetable oils as a cooling medium in comparison to a standard mineral oil, *J. Mat. Eng. and Perf.*, vol. 8, no. 4, p. 409-416.
- [17] Honary, L.A.T. (1999) Soybean based hydraulic fluid, *U.S. Patent 5,972,855*.
- [18] Christie, W.W. (1989) *Gas Chromatography and lipids: a practical guide*, The Oily Press, Bridgwater, p. 11-27, 69.
- [19] Neto, P.R. (2000) Biofuel production alternative to diesel oil obtained by the transesterification of the soybean oils used to food, *Química Nova*, São Paulo, vol. 23, no. 4, p. 531-537. (in Portuguese)
- [20] Liscic, B., Tensi, H.M., Totten, G.E., Webster, G.M. (2003) Non-lubricating process fluids: Steel quenching technology, *Fuels and Lubricants Handbook Technology, Properties, Performance and Testing*, ASTM International, West Conshocken, PA., p. 587-634.
- [21] Tensi, H.M., Steffen, E. (1985) Measuring of the quenching effect of liquid hardening agents on the basis of synthetics, *Steel Research*, vol. 56, p. 489-496.
- [22] Kobasko, N.I., Totten, G.E. (2004) Design of the industrial quenching processes, *Transactions of Materials and Heat Treatment*, vol. 25, no 5, p. 527-530.
- [23] Aronov, M.A., Kobasko, N.I., Powell, J.A., Hernandez-Morales, J.B. (2008) Correlation between Grossmann H – Factor and generalized biot number Bi_v , *Proc. of the 5th WSEAS Int. Conf. on Heat and Mass Transfer (HMT'08)*.
- [24] Kobasko, N. (2008) Hardness and structure prediction at the core of any steel part using Jominy standard test, *Proc. of the 5th WSEAS Int. Conf. on Heat and Mass Transfer (HMT'08)*.
- [25] Canale, L.C.F., Kobasko, N.I., Totten, G.E. (2007) Intensive Quenching: Part 1 – What is it?, *International Heat Treatment and Surface Engineering*, vol. 1, no. 1, p. 30-33.
- [26] Schneider, M. (2002) *Government Industry Forum on Non-food Uses of Crops [GIFNFG 7/7] –Case Study Plant Oil Based Lubricants in Total Loss and Potential Loss Applications*, Final Report, University of York, England.

- [27] Kodali, D.R. (2002) High Performance Ester Lubricants from Natural Oils, *Industrial Lubrication and Tribology*, vol. 54, no. 4, p. 165 - 170.
- [28] Santos, J.C.O., Santos, I.M.G., Souza, A.G. (2005) Effect of heating and cooling on rheological parameters of edible vegetable oils, *J. of Food Engineering*, vol. 67, p. 401-405.
- [29] Fasina, O.O., Hallman, H., Craig-Schmidt, M., Clements, C. (2006) Predicting temperature-dependence viscosity of vegetable oils from fatty acid composition, *J. Am. Oil Chem.Soc.*, vol. 83, no. 10, p. 899-903.
- [30] Adhvaryu, A., Erhan, S.Z., Liu, Z.S., Perez, J.M. (2000) Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy, *Thermochemica Acta*, , vol. 364, p. 87-97.