

# EPOXIDIZED SOYBEAN OIL: EVALUATION OF OXIDATIVE STABILIZATION AND METAL QUENCHING/HEAT TRANSFER PERFORMANCE

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**Abstract.** *Vegetable and animal oils as a class of fluids have been used for hundreds of years, if not longer, as quenchants for hardening steel. However, when petroleum oils became available in the late 1800s and early 1900s, the use of these fluids as quenchants, in addition to their use in other industrial oil applications quickly diminished. This was primarily, but not exclusively, due to their generally very poor thermal-oxidative instability and the difficulty for formulating fluid analogs with varying viscosity properties. Interest in the use of renewable fluids, such as vegetable oils, has increased dramatically in recent years as alternatives to the use of relatively non-biodegradable and toxic petroleum oils. However, the relatively poor thermal-oxidative stability has continued to be a significant reason for their general non-acceptance in the marketplace. Soybean oil is one of the most highly produced vegetable oils in Brazil. Currently, there are commercially produced epoxidized versions of soybean oil which are available. The objective of this paper is to discuss recently obtained results showing the dramatic improvement in thermal-oxidative stability of epoxidized soybean oils and to discuss their potential use and heat transfer properties as viable alternatives to petroleum oils for hardening steel.*

**Keywords:** *epoxidized soybean oil, oxidative stability, quenchants*

## 1. INTRODUCTION

Hardening steel occurs by first heating the steel to the specified austenitizing temperature, typically in the range of 750-1100°C and cooling it in such a way that the desired microstructure is formed obtaining required properties such as hardness, strength, and toughness. The main objective of any quenchant is to produce the desired metallurgical transformations. In addition, the quenchant must prevent cracking and minimize distortions due to non-uniform heat transfer over the surface of the steel.

The microstructures that are formed during quenching depend on the heat transfer properties at the hot metal interface. The cooling time-temperature pathway is designated as the cooling curve. One method of illustrating the steel transformation microstructures during the quenching process is to superimpose the cooling time-temperature curve for steel cooled in a specific quenching medium over a TTT (Time-Temperature-Transformation) or CCT (Continuous-Cooling-Transformation) curve for the steel of interest.

The most common quenchants, depending on the steel and hardening process, include: air, petroleum oil, water, brine, aqueous polymer solutions and high-pressure gas quenching. Of the vaporizable quenchants, petroleum oil derived fluids are the most commonly encountered throughout the industry.

The challenge to replace petroleum basestocks due to potential problems with long-term availability in addition to the relative toxicity and poor biodegradability has done the vegetable oils as interesting alternative because their biodegradable, environmentally friendly and non-toxic renewable basestocks. Beyond these characteristics vegetable oil have good anti-friction properties, low volatility, high viscosity index, and good miscibility with other fluids (Adhvaryu and Erhan, 2002).

Although the potential use of vegetable oils as basestocks for industrial oil formulation continues to be of interest, they possess a number of very substantial limitations, not the least of which is relatively poor thermal-oxidative stability relative to petroleum oil-derived formulations. For example, vegetable oils typically cannot withstand reservoir temperatures in excess of 80°C due to the onset of oxidation, although the use of antioxidants can partially offset this notable limitation (Goyan *et al.*, 1995; Zeeman *et al.*, 1998). Oxidation limits the useful life vegetable oil-derived fluids because of the increased viscosity that results which is further accelerated by elevated temperatures and contact with

metals such as iron and copper (Ruger *et al.*, 2002). Adhvaryu *et al.* (2000) have concluded that soybean oil oxidizes at a rate that is at least an order of magnitude greater than that of petroleum oil.

Thermo-oxidative stability of a vegetable oil is dependent on the fatty ester composition of the triglyceride structure. Increasing amounts of unsaturation in the fatty ester structure leads to increased oxidative instability. Schneider (2002) and Kodali (2002) have reported that the relative rate of oxidation increases as the number of double bonds in conjugation with each other increases in the following relative order: stearic (1) < oleic (10) < linoleic (100) < linolenic (200) shown in Fig 1.

Knothe (2005) reported that the initiation step of oxidative degradation involves hydrogen abstraction from fatty ester of the lipid by an initiator. The most favored position for hydrogen abstraction occurs with the lowest activation energy which is an allylic methylene, the (CH<sub>2</sub>) adjacent to the CH=CH moiety, and the allylic radical that is formed is stabilized by resonance over the double bond structure and the resonance stabilization increases with the number of double bonds in conjugation. Bis-allylic positions in polyunsaturated fatty acids such as linoleic acid (double bonds at Δ9 and Δ12, giving one bis-allylic position at C-11) and linolenic acid (double bonds at Δ9, Δ12, and Δ15, giving two bis-allylic positions at C-11 and C-14), are even more prone to autoxidation than the allylic position of oleic acid as indicated in Fig. 1.

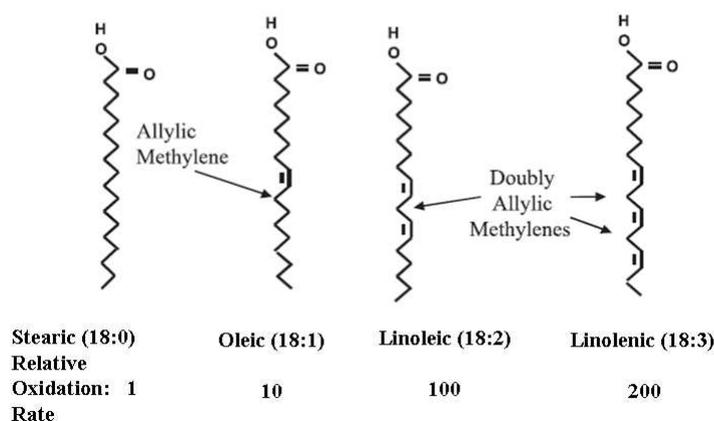


Figure 1. Allylic methylene functionality: linolenic > linoleic > oleic

Souza *et al.* (2009) reported that although selection of the most effective antioxidants do provide substantially improved inhibition to oxidation, this is insufficient to rival the oxidative stability possible with the use of petroleum oil-based fluids. Clearly, something significantly more effective is needed to provide the necessary oxidative stability for applications where the fluid will be subjected to relatively high, even if only for a short-time, thermal excursions.

Others possibilities to improve the thermo-oxidative stability of the vegetable oils are genetic and chemical modification. Modification of the chemical structure of vegetable oils has been proposed for the development of environmental friendly vegetable-oil derived basestocks. One modification of vegetable oil structure that has proposed is epoxidation. Figure 2 provides a generic illustration of a fully epoxidized soybean oil. Double bond epoxidation has been utilized for over 50 years as described by Julian *et al.* (1956) and Findley *et al.* (1962). Epoxidized vegetable oils are of potentially great interest for commercial applications as lubricants, synthetic detergents, and for the production of polyurethane foams.

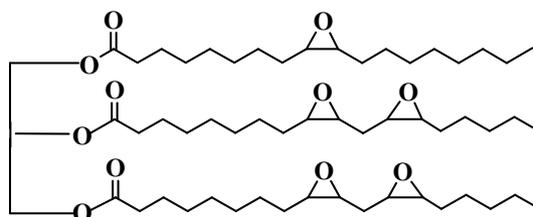


Figure 2. Generic simplified illustration of one potential component in epoxidized soybean oil, adapted from Hwang and Erhan (2006).

Wu *et al.* (2000) showed that epoxidized rapeseed oil exhibited greater oxidative stability than unepoxidized rapeseed oil without chemical modification. Moreover, the epoxidation treatment did not modify the biodegradability of the base stock.

Adhvaryu and Erhan (2002) and Erhan *et. al.* (2003) reported that epoxidized soybean oil demonstrated improved thermal and oxidative stability relative to unepoxidized soybean oil and genetically modified high oleic soybean oil in certain high temperature lubricant applications.

Epoxidation has been shown to significantly improve oxidative stability relative to unepoxidized triglyceride structure. Only limited data is available comparing the resulting oxidative stability of the epoxidized triglycerides with their functionally equivalent petroleum oil basestocks.

The objective of this paper is to discuss recently obtained results showing the dramatic improvement in thermal-oxidative stability of epoxidized soybean oils and to discuss their potential use and heat transfer properties as viable alternatives to petroleum oils for hardening steel.

## 2. EXPERIMENTAL PROCEDURES

The epoxidized soybean oil used in this work was obtained from Inbra (Indústrias Químicas Ltda) and was designated as ESBO. The soybean oil, produced by Cargill Agrícola S/A, was purchased at a local market in São Carlos/SP, Brazil and was commercially designated as Liza and classified as “pure” soybean oil (SO). In addition, one Fatty Acid Methyl Ester (FAME) derivative of soybean soapstock designated as FAME 3P was obtained from Cognis do Brasil Ltda. (Soybean oil soapstock is a by-product of the caustic refining process of soybean oil.) A reaction schematic illustrating the general synthesis of FAME from a triglyceride such as soybean oil is shown in Fig. 3. The FAME 3P was added with stirring into ESBO producing the formulations designated in Tab.1.

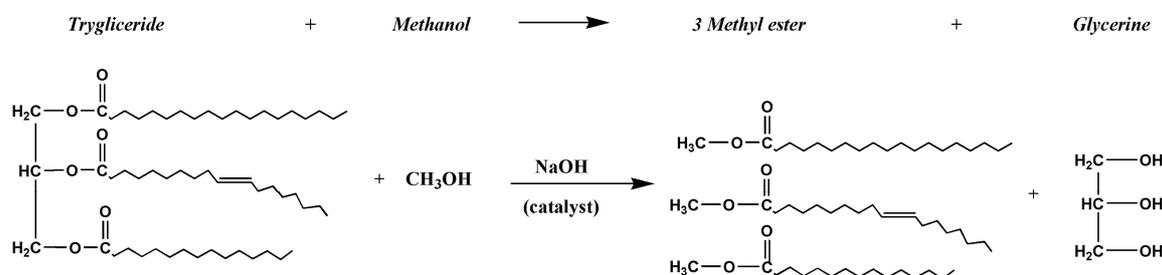


Figure 3. General illustration of the synthesis of a FAME derivative from a triglyceride.

Table 1. ESBO\_I and FAME formulations using for thermal-oxidation study.

Designation	% ESBO	%FAME
ESBO	100	0
EF 30	70	30
EF 38	62	38
EF 60	40	60
FAME	0	100

Two fully-formulated, commercially available, petroleum-based quench oils used for comparison were: Lubrifort Temp 4 (conventional “slow” oil) and Lubrifort Temp 2 (accelerated “fast” oil). These petroleum-based quench oils were obtained from Quimifort Indústria e Comércio Ltda., São Carlos, SP, Brazil.

Viscosity was measured at 40°C and 100°C using calibrated Cannon-Fenske viscometer tubes according to ASTM D445-06 “Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)”. The viscosity index was calculated according to ASTM D2270-10 “Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40° and 100°C”. All viscosity measurements were run in duplicate and the average value was reported.

Cooling curves were obtained at 60°C, non-agitated condition, according to ASTM D6200 “Standard Test Method for Determination of Cooling Characteristics of Quench Oils by Cooling Curve Analysis”. This method 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 were recorded at selected time intervals to establish a cooling temperature versus time curve. All measurements were performed in duplicate and averaged. The averaged data are reported here.

## 3. RESULTS AND DISCUSSION

### 3.1. Viscosity Properties

The viscosity-temperature relationship is an important physical property for any potential basestock that may be used for steel quenchant formulations since heat transfer is exponentially related to the viscosity of the heat transfer medium. As steel cools, the viscosity at the interface between the cooling metal surface and the bulk fluid decreases and the interfacial heat transfer coefficient which is partly determined by the structurally dependent, viscosity-temperature relationship of the basestock will control the time-temperature (cooling curve) exhibited by the quenchant which, in turn, controls the overall hardening properties of the quenching medium. According to Santos *et. al.* (2005), the viscosity of the triglyceride components of the vegetable oil increases with the fatty acid ester chain length and decreases with the amount of unsaturation in the fatty acid ester alkyl chain.

Viscosity-temperature properties of a fluid is characterized by the so-called viscosity index (VI) which is an arbitrary measure of the change of viscosity with respect to temperature and is commonly used to characterize oil basestocks. VI provides a numerical comparison of the viscosity of a fluid at two different temperatures. Although there are various numerical correlations to characterize the viscosity-temperature of a lubricant, some of which were summarized by O'Donnell and Zakarian (1984), the classic relationship is the Walther equation (Sánchez-Rubio, J. *et.al.* 2006):

$$\log \log (\nu+0.7) = A - B \log T \quad (1)$$

where:  $\log$  is the logarithm to the base 10,  $\nu$  is the kinematic viscosity ( $\text{mm}^2/\text{s}$ ) (cSt) and  $T$  is the absolute temperature (K) – ( $K = t + 273$ ) and  $t$  is the temperature in  $^{\circ}\text{C}$ . The values  $A$  and  $B$  are constants. The constant 0.7 in Eq. 1 is the value most often used for petroleum-based lubricants. However, different values of this constant may be determined for different lubricants to improve the data fit, if required. ASTM D341-09 “Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products” is an industrial standard used to represent the change of viscosity of petroleum products with the temperature and it is based on Walther equation Eq. (1).

According to ASTM D341, kinematic Viscosity data obtained by ASTM D445 is determined at two temperatures,  $40^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  and the data is plotted as shown in Fig. 4. The variation in slope of the lines summarized in Tab. 2 indicates the relative change of viscosity with respect to temperature within the range of  $40^{\circ}\text{C}$  -  $100^{\circ}\text{C}$ . The slope of the lines in Figure 4 and the Walter B slope coefficients show that the change in viscosity with respect to temperature of the ESBO/FAME blends progressively decreases as the amount of FAME in the blend increases which is not unexpected because the viscosity range at both  $40^{\circ}\text{C}$  and also  $100^{\circ}\text{C}$  decreases with increasing FAME content in the blend. Interestingly, although the change in viscosity with respect to temperature of the fast petroleum oil-derived quenchant (Temp 2) is less than the slow analog (Temp 4). However, as indicated in the previous discussion, these data suggest that a different numerical constant in the viscosity parameter, other than 0.7, may be required when the Walther equation is used for vegetable oil and vegetable oil-derived basestocks. This was not examined as part of this work.

Viscosity indexes are currently most commonly determined according to ASTM D2270 and the VI value is determined from the appropriate look-up table. Alternatively, internet calculators such as one published by Evonik RhoMax may also be used (Anon., 2011).

The results of kinematic viscosity measurements and the calculated viscosity index (VI) obtained for each formulation and the two petroleum oil quenchants are shown in Tab. 2. The viscosity of epoxidized soybean oil (ESBO), at both temperatures, is higher than the other formulations and as reported in previous study described in literature (Adhvaryu and Erhan, 2002). FAME exhibited the lowest viscosity compared with the other formulations, as expected since it is a relatively low molecular weight monoester. Also, increasing amounts of FAME addition to the ESBO resulted in a progressive viscosity decrease. The reason for performing this study was to examine the potential use of FAME addition to decrease the otherwise extraordinarily high viscosity of ESBO which would inhibit its potential use as a quenchant. These data show that, as expected, the addition of FAME to ESBO can be performed to obtain reasonably similar viscosity properties relative to unadulterated soybean oil. However, the viscosity data of the ESBO/FAME blends do not compare well with either petroleum oil quenchant evaluated.

The viscosity of the slow oil was considerably greater than either the soybean oil or most of the ESBO blends. The viscosity of the fast oil was substantially lower than either the slow oil or soybean oil. The viscosities of EF 60 blend was similar to the fast petroleum oil quenchant (Temp 2) at  $40^{\circ}\text{C}$ , and the viscosity of EF 30 blend approximated the slow petroleum oil quenchant (Temp 4). Interestingly, while it is possible to blend ESBO/FAME to obtain the viscosity of either the fast or slow oil at  $40^{\circ}\text{C}$ , it is not possible to match the viscosities at both  $40^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ .

The reason for the inability to match the viscosity properties of these blends with the petroleum oil quenchants is due to the substantially different VI properties of these fluids. Table 2 shows that the VI of soybean oil (229) was significantly higher than either the fast (143) or slow (99) petroleum oil and the VI of the fast oil was nearly 50% greater than that of the slow oil. These values represent the expected change in viscosity of the oil with change in temperature and the lower the VI value, the greater the change that is expected. FAME had the highest VI (347) of the fluids evaluated, even greater than soybean oil, and the value for ESBO (141) was similar to that published previously (142) (Doll *et. al.*, 2008). Increasing amounts of FAME in an ESBO/FAME blend resulted in a progressively increasing VI. It should be noted that a comparison of the viscosity properties of the fast and slow petroleum quench oils indicates that the basestocks are different for these two oils. The slow oil possesses a substantially greater fluid viscosity which would be expected to result in generally slower cooling rates throughout the quenching process relative to the fast oil since heat transfer decreases with increasing viscosity.

Table 2. Kinematic viscosity and viscosity index (VI) determined for every formulations and petroleum oil based quenchants.

Physical Property	Soybean Oil, Epoxidized Soybean Oil (ESBO), FAME and ESBO/FAME Blends						Petroleum Oil Quenchant	
	SO	ESBO	EF 30	EF 38	EF 60	FAME	Slow Oil	Fast Oil
							Temp 4	Temp 2
Viscosity (cSt at 40°C)	31.71	162.77	48.65	37.43	16.25	4.76	52.86	16.96
Viscosity (cSt at 100°C)	7.74	19.91	9.48	8.11	4.57	2.02	7.38	4.05
Walther slope (“B”)	0.392	0.572	0.464	0.435	0.347	0.097	0.518	0.362
Viscosity Index	229	141	183	199	220	347	99	143

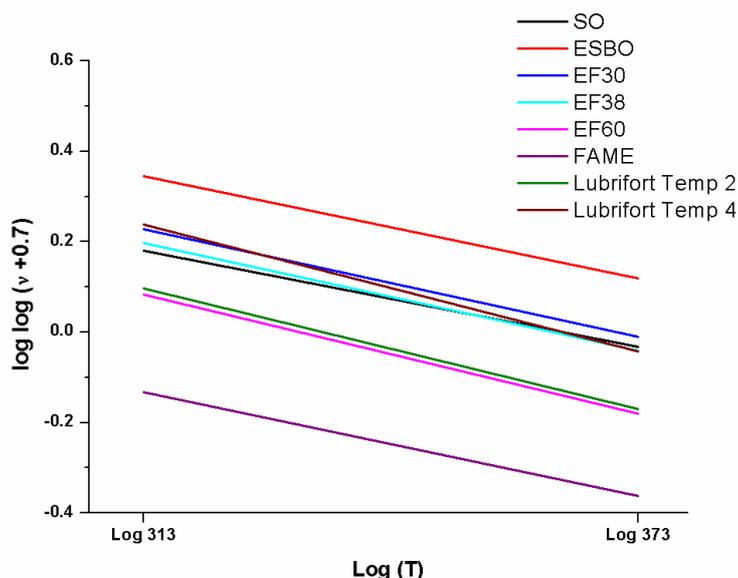


Figure 4. Viscosity-Temperature property comparison of each fluid (SO - soybean oil, Lubrifort Temp 2 - fast oil, Lubrifort Temp 4 – slow oil and ESBO - epoxidized soybean oil/FAME blend – see Tab. 1) studied showing the greater viscosity ( $\nu$ ) – absolute temperature (K) sensitivity.

### 3.2. Quenching/Heat Transfer Performance

Quenching cooling times and cooling rates and heat transfer coefficients for each fluid evaluated in this work were determined by cooling curve analysis under unagitated conditions according to ASTM D6200 at a bath temperature of 60°C. Two petroleum-based quenchants were used for comparison: Lubrifort Temp 2 (fast oil) and Lubrifort Temp 4 (slow oil). The “slow” and “fast” oil designations typically refer to the film-boiling/nucleate boiling properties of a quenchant. When hot ( $\approx 850$  °C) steel (or Inconel) is immersed into a vaporizable fluid such as a petroleum oil, the hot surface is surrounded by a vapor blanket and heat transfer occurs by a full-film boiling mechanism. Heat transfer through this vapor blanket is typically the slowest encountered in the process. Upon further cooling, the film collapses and nucleate boiling results. The transition between full-film boiling and nucleate boiling is designated as the Leidenfrost temperature and heat transfer is typically fastest in this region. When the temperature decreases to a temperature less than the boiling point of the components of the oil, heat transfer occurs predominantly by convection which is considerably slower than nucleate boiling but faster than full-film boiling. “Fast” quench oils typically contain additives that facilitate the rupture of the vapor blanket.

Since nucleate boiling is facilitated at a higher temperature (shorter time), such oils are used to harden otherwise difficult to harden steels such as carbon steels and low-hardenability alloy steels. Because nucleate boiling occurs sooner than would be observed for a slow oil (with an otherwise identical composition and physical properties) it is designated as a “fast” quenching oil. Figs. 5 and 6 show the cooling time-temperature curves and cooling rate curves for the fluids evaluated as part of this work. The cooling curve parameters for the fluids evaluated in this work are summarized in Tab. 3.

Table 3. Cooling parameters obtained by ASTM D6200 at 60°C bath temperature and with no agitation.

Cooling Curve Parameters obtained at 60°C bath temperature	Soybean Oil, Epoxidized Soybean Oil (ESBO), FAME and ESBO/FAME Blends						Petroleum Oil Quenchant	
	SO	ESBO	EF 30	EF 38	EF 60	FAME	Slow Oil	Fast Oil
							Temp 4	Temp 2
$CR_{700^{\circ}C}$ (°C/s)	94.87	90.35	27.47	23.26	24.23	25.53	74.96	32.98
$CR_{300^{\circ}C}$ (°C/s)	15.60	8.18	11.89	12.90	18.97	19.31	5.50	5.81
$CR_{200^{\circ}C}$ (°C/s)	3.00	3.03	2.67	2.77	3.32	3.57	2.98	2.70
$t_{700^{\circ}C}$ (s)	4.80	5.14	6.58	7.47	6.82	6.29	6.08	7.37
$t_{300^{\circ}C}$ (s)	13.53	15.83	16.31	16.80	14.66	16.70	23.22	18.72
$t_{200^{\circ}C}$ (s)	28.94	40.64	28.94	36.22	29.84	31.15	51.78	42.20

Heat Transfer Properties	Soybean Oil, Epoxidized Soybean Oil (ESBO), FAME and ESBO/FAME Blends						Petroleum Oil Quenchant	
	SO	ESBO	EF 30	EF 38	EF 60	FAME	Slow Oil	Fast Oil
							Temp 4	Temp 2
Heat transfer coefficient (W/m <sup>2</sup> K) at 700 °C	2398	2398	719	525	547	1008	1919	744
Heat transfer coefficient W/m <sup>2</sup> K at 300 °C	803	494	659	664	977	1154	283	330
Heat transfer coefficient (W/m <sup>2</sup> K) at 200 °C	296	264	233	241	289	311	260	235

The first comparison to be discussed is for the “fast” and “slow” petroleum oil. When evaluating these results, it is important to consider the viscosity and viscosity index relationships shown in Tab. 2 which suggest that these two quench oils are formulated using substantially different basestock with the “fast” quench oil (Temp 2) being formulated with a relatively low viscosity (16.06 cSt) versus 52.86 cSt viscosity for the “slow quench oil (Temp 4). This complicates the cooling curve comparison of the two quench oils. Table 3 shows that the cooling rate at the higher 700 °C temperature ( $CR_{700^{\circ}C}$ ) is much faster for the slow oil and the time to cool to 700 °C ( $t_{700^{\circ}C}$ ) is somewhat faster. Furthermore, inspection of the cooling time-temperature and cooling rate curves do not exhibit the substantially reduced full-film boiling region more conventionally expected for fast oil compared to slow quenching oil. In fact, the slow quenching oil, even at the higher viscosity, did not exhibit the expected extended full-film boiling. The cooling rate at 300 °C ( $CR_{300^{\circ}C}$ ) was essentially equivalent for both oils. However, the cooling times to 300 °C ( $t_{300^{\circ}C}$ ) and 200 °C ( $t_{200^{\circ}C}$ ) are substantially slower for the slow quench oil relative to the fast oil which is the expected behavior.

The next comparison to be performed relative to the fast and slow petroleum oil quenchant is soybean oil. Inspection of the soybean oil cooling time-temperature and cooling rate curves, shows that it does exhibit a minimal vapor blanket cooling region which typically accompanies full-film boiling. However, the cooling curve parameters for soybean oil in Tab. 4 shows that it exhibits substantially faster values for both  $CR_{700^{\circ}C}$  and  $t_{700^{\circ}C}$  relative to either petroleum oil quenchant suggesting that cooling process for soybean oil is probably predominated by convection. The  $CR_{300^{\circ}C}$  and  $t_{300^{\circ}C}$  is also much faster than either the fast or slow oil. While the  $CR_{200^{\circ}C}$  and  $t_{200^{\circ}C}$  is also faster than either petroleum oil, the difference is considerably less. Overall, the soybean oil is clearly the fastest of the quenchant evaluated.

When comparing the cooling time-temperature and cooling rate curves for FAME (which is the methyl ester of fatty acid components derived from methanolysis of soybean oil) it is important to realize that FAME is composed of monoesters which represent a much lower molecular weight and consequently is correspondingly more volatile than soybean oil which is a triglyceride (triesters). Comparison of the cooling time-temperature curve and cooling rate curve for FAME shows that it exhibits a substantially longer vapor blanket (full-film boiling) region than either soybean oil or either petroleum oil quenchant. The data in Tab. 4, shows that the  $CR_{700^{\circ}C}$  is much slower than soybean oil and the cooling rates at  $CR_{300^{\circ}C}$  and  $CR_{200^{\circ}C}$  are faster than soybean oil, although the differences may not be significant. Although the cooling rate 700 °C is slower due to the full-film boiling process, the cooling rates at 300 °C and 200 °C are faster for FAME than those exhibited by either the fast or slow petroleum oil. The cooling time at 700 °C is very similar for FAME and the petroleum oil quenchant although the cooling times are faster for FAME at 300 °C and 200 °C.

The  $CR_{700^{\circ}C}$  for ESBO is approximately the same as soybean cooling rate at this temperature; it exhibits a very minimal apparent vapor blanket region. In view of the expected very high boiling points for both soybean oil and ESBO and the corresponding low vapor pressure, it is likely that the cooling process for ESBO is also predominated by convection. The  $CR_{300^{\circ}C}$  is much less for ESBO than soybean oil which is likely due to the much higher viscosity of ESBO (162.8 cSt) compared to soybean oil (31.7 cSt). The  $t_{700^{\circ}C}$  and  $t_{300^{\circ}C}$  is slightly longer for ESBO than soybean oil although the  $t_{200^{\circ}C}$  is much longer for ESBO. Compared to FAME, the  $CR_{700^{\circ}C}$  is much faster because FAME exhibits a

prolonged vapor blanket cooling region which is not observed for ESBO. The  $t_{700^{\circ}\text{C}}$  and  $t_{300^{\circ}\text{C}}$  is faster for ESBO but ESBO has a longer  $t_{200^{\circ}\text{C}}$ . ESBO cools much faster to 700 °C than either petroleum oil and is also faster at 300 °C, although it is only marginally faster at 200 °C. The  $t_{700^{\circ}\text{C}}$  and  $t_{300^{\circ}\text{C}}$  are faster for ESBO than either petroleum oil. Although the  $t_{200^{\circ}\text{C}}$  is faster for ESBO than the slow petroleum oil, the values for  $t_{200^{\circ}\text{C}}$  are approximately comparable for ESBO and the fast petroleum oil.

The reason for doing this work was to determine if it is possible to reasonably match the quenching performance of a petroleum oil, whether fast or slow, or both, by blending FAME and epoxidized soybean oil (ESBO). The approach used to address this question was to blend different ratios of FAME and ESBO and compare the quenching properties with the fast and slow petroleum oil quenchants used for this study. Careful inspection of the cooling time-temperature and cooling rate curves shows that the vapor blanket cooling region was significantly extended relative to soybean oil and ESBO but somewhat less than that observed for FAME. However, the vapor blanket regions exhibited by EF 30, EF 38 and EF 60 were intermediate between FAME and ESBO but quite similar to each other. The  $CR_{700^{\circ}\text{C}}$  of the FAME and EF 30, EF 38 and EF 60 blends were comparable and were also slower than ESBO and both the fast and slow petroleum oil. The  $CR_{300^{\circ}\text{C}}$  followed the trend:

$$\text{ESBO} < \text{EF 30} < \text{EF 38} < \text{EF 60} < \text{FAME}$$

This trend was directly proportional to decreasing fluid viscosities. No similar identifiable trend was observed for  $CR_{200^{\circ}\text{C}}$ . In addition, none of the cooling times followed any significant trend. Finally, and importantly, none of the ESBO/FAME blends produced cooling curve time and rate parameters that matched well with the fast and slow petroleum oils used for this work. The reasons for this are varied but perhaps one of the most important is the inherent film boiling properties that seemed to be exhibited by FAME and its blends. This was further complicated by the varying viscosities exhibited by the blends.

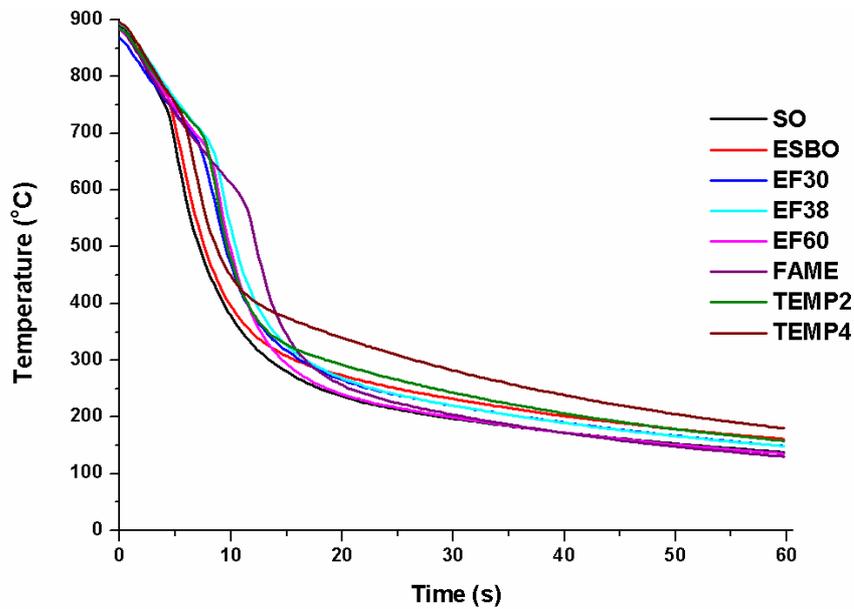


Figure 5. Cooling curves data at 60 °C bath temperature with no agitation.

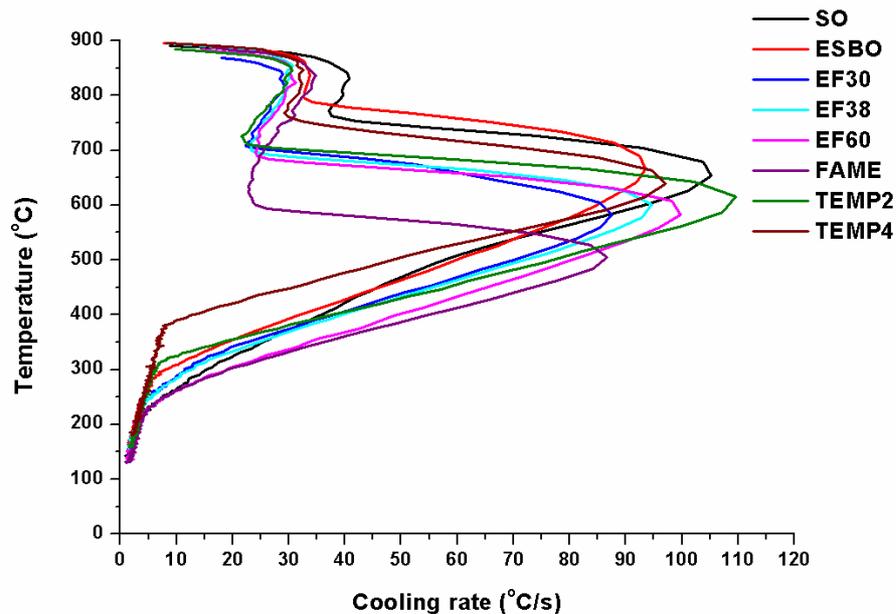


Figure 6. Cooling rates data at 60 °C bath temperature with no agitation.

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 the ASTM D6200 standard 12.5 mm dia x 60 mm cylindrical Inconel 600 probe provides cooling rate and temperature vs. time at the core of probe, it is only possible to evaluate “average effective heat transfer coefficients” which are used in the heat treating industry. During quenching, the heat transfer coefficient is dependent on: surface temperature of the steel part (probe), 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 ( $\alpha$ ). During nucleate boiling and convective cooling, average effective heat transfer coefficients can be determined. In this paper, heat transfer coefficients were calculated according to the theory of regular conditions and the calculation procedure described previously by Kobasko *et. al.* (2010) was used and will not be discussed further here.

The heat transfer coefficients obtained showed that the heat transfer coefficient at 700 °C ( $\alpha_{700^{\circ}\text{C}}$ ) for the slow petroleum oil was more than twice as fast as the fast petroleum oil. The values for soybean oil and ESBO were the same and were substantially faster than the other fluids evaluated. The  $\alpha_{700^{\circ}\text{C}}$  for FAME was slower than soybean oil and ESBO and which was intermediate between the fast and slow petroleum oil. The  $\alpha_{700^{\circ}\text{C}}$  values for the blends and were slower than for the fast petroleum oil and FAME which is probably attributable to the increasing viscosity relative to FAME. At 300 °C, the  $\alpha_{300^{\circ}\text{C}}$  value for soybean oil was much faster than that for ESBO which was due to the substantially lower fluid viscosity. The  $\alpha_{300^{\circ}\text{C}}$  value for the slow oil was lower than that for the fast oil which was also due to the greater viscosity of the slow oil. The  $\alpha_{300^{\circ}\text{C}}$  value for FAME was fastest due to its low viscosity and the  $\alpha_{300^{\circ}\text{C}}$  values for the blends were intermediate between the values for ESBO and FAME. Finally, the heat transfer coefficients at 200 °C ( $\alpha_{200^{\circ}\text{C}}$ ) for all of the quenchants were similar. On the basis of these data, it is suggested that comparison of the heat transfer coefficients provides the least ambiguous and most insightful results with respect to quenching performance.

#### 4. CONCLUSION

The metal quenching performance of epoxidized soybean oil was compared with both unepoxidized soybean oil (ESBO) and two fully formulated, commercially available, petroleum-based “fast” and “slow” quench oils. This study showed:

1. The very high viscosity of ESBO would preclude its use as a quench oil.
2. FAME derived from soybean oil reduces the viscosity of ESBO to reasonably model a petroleum oil-based quenchant.
3. Quenching performance of soybean oil was evaluated by cooling curve analysis which suggests that heat transfer occurs predominantly by convection as does ESBO. However, the heat transfer mechanism of FAME and FAME/ESBO blends occurs by three: film-boiling, nucleate boiling and convection.
4. Further work is required to more fully assess the comparability of FAME/ESBO blends with respect to formulated petroleum oil-based quenchants currently in use.

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