EFFECTS OF SYNTHETIC GLYCERYL ESTER ADDITIVES ON COLD FLOW PROPERTIES OF DIESEL OIL

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ผลของสารเติมแต่งกลีเซอริลเอสเทอร์สังเคราะห์ต่อสมบัติการไหลที่อุณหภูมิต่ำของน้ำมันดีเซล

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ฤชาพงษ์ กวีวุฒเฑ์ : ผลของสารเติมแต่งกลีเซอริลเอสเทอร์สังเคราะห์ต่อสมบัติการไหลที่อุณหภูมิ ต่ำของน้ำมันดีเซล. (EFFECTS OF SYNTHETIC GLYCERYL ESTER ADDITIVES ON COLD FLOW PROPERTIES OF DIESEL OIL) อ.ที่ปรึกษาหลัก : ผศ. ดร.วรินทร ชวศิริ

การสังเคราะห์กลีเซอริลเอสเทอร์ซึ่งเป็นสารอนุพันธ์ของโซคีทัลและกรดไขมันที่สนใจ (กรดสเตียริก กรดปาล์ มิติก กรดลอริก กรดไมริสติก กรดโอเลอิกและกรดลิโนเลนิก)เพื่อศึกษาสมบัติการไหลที่อุณหภูมิต่ำด้วยจุดไหลเทของน้ำมัน ดีเซลเมื่อเติมสารกลีเซอรัลเอสเทอร์สังเคราะห์ ซึ่งสารกลีเซอรัลลอเรทความเข้มข้น 1,000 มก./กก. ในน้ำมันดีเซลมี ประสิทธิภาพสูงสุดในการลดจุดไหลเทโดยลดลงได้ 3 °C แต่น้ำมันดีเซลที่เติมสารกลีเซอรัลลอเรทความเข้มข้น 1,000 มก./กก. ลักษณะปรากฏเป็นน้ำมันขุ่นที่อุณหภูมิห้อง จึงไม่สามารถใช้เป็นน้ำมันดีเซลเชิงการค้าได้ เมื่อนำสารติมแต่งทาง การค้า 200 มก./กก. และสารกลีเซอรัลลอเรท 100 มก./กก. ในน้ำมันดีเซลสามารถลดจุดไหลเทจาก 13.5 °C เป็น 3 °C ซึ่งลดจุดไหลเทได้มากกว่าการเติมสารเติมแต่งทางการค้า

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The synthesis of solketal derivatives with some selected fatty acid (stearic acid, palmitic acid, lauric acid, myristic acid, oleic acid and linolenic acid) to glyceryl esters was conducted. All compounds were characterized by spectroscopic means. Cold flow properties of diesel oil with these glyceryl ester additives were studied in terms of pour point (PP). Glyceryl laurate was the most effective pour point decreasing at 1,000 mg/kg (DPP = 3°C). However, the blended diesel of 1,000 mg/kg glyceryl laurate could not commercialize finishing product because that was hazy diesel at room temperature. The combination of glyceryl laurate and commercial additive was discovered. Moreover, the pour point result of diesel with combination additive more decreased than blended diesel only commercial additive. 200 mg/kg of commercial and 100 mg/kg of glyceryl laurate show reduced pour point of diesel from 13.5 °C to 3 °C.
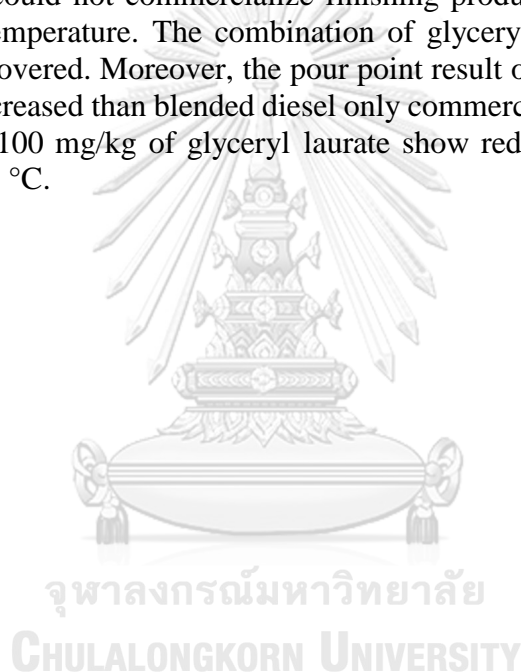
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LIST OF ABBREVIATIONS

CFPP	Cold Filter Plugging Point
CO	Carbon monoxide
CP	Cloud Point
cSt	Centistoke
^{13}C-NMR	Carbon-13 (C13) Nuclear Magnetic Resonance
°C	Degree Celsius
d	doublet
g/cm3	gram per centimeter cube
Hz	Hertz
^{1}H-NMR	Proton-1 (H1) Nuclear Magnetic Resonance
J	Coupling Constant
m	multiplet
mg/kg	milligram per kilogram
min.	minute
NOx	Nitrogen Oxide
PP	Pour Point
PPD	Pour Point Depressant
ppm	part per million
ΔPP	Differential of pour point
q	quartet
s	singlet
WAT	Wax Appearance Temperature
%wt., %w/w	percent by weigh
%w/v	percent weigh by volume
δ	Chemical shift
δ_H	Chemical shift of proton

CHAPTER 1

INTRODUCTION

Nowadays alternative fuel is supported by Thai government policy. This pushes to utilize agricultural products for supplying to alternative fuel production. Biodiesel from palm has been known as an alternative fuel for blending or substitution in petroleum diesel. Biodiesel has been produced in high rate to Thai government policy fulfillment. Biodiesel is not only a major product from trans-esterification of used vegetable oil, but also producing a lot of glycerol at the same number of biodiesel requirement. Glycerol has widely been used in various industries such as cosmetic, pharmaceutical etc.; nonetheless cannot use all. Some amounts of glycerol are used for moisturized enhancement agent in skin care, eye drop, pill coating even bakery sweetening. The other way for using glycerol as raw material is interesting for further exploration.

Petroleum industry is a top demand in Thailand. More than 70 million liters has been used for transportation[1]. The first list of usage is diesel that is basic transport fuel. Diesel form crude oil was from petroleum industrial process and adjusted some quality before customer distribution station. The diesel quality must be following the High-speed diesel standard properties from Department of Energy Business announcement (Thailand): Characteristic and Property requirements of Diesel 2019 (publication date: May 14, 2019)[2] (Table 1). A concerned property of diesel is pours point. Because that temperature can be indicated appearance and flowability of diesel. Pour point improvement of diesel can be simply accomplished by blending with miscible additives. Those additives must maintain characteristics of diesel. The commercial pour point additives are mainly long chain polymers which are designed for cold flow properties improvement in crude oil. Once that additive was added in diesel, polymer can be uncompleted combustion and engine inhibition.

From above, this research aims to use modified glycerol as pour point additive for diesel. The first step, glycerol will transform to solketal. Synthetic pour point

additives were then synthesized with some selected fatty acids. Finally, that synthetic additive application was proved by blending with diesel.

Table 1.1 High-speed diesel standard properties from Department of Energy Business announcement (Thailand): Characteristic and Property requirements of Diesel 2019 (Publication date: May 14, 2019)

Item	Method	Unit	Range
Specific Gravity at 15.6/15.6 °C	ASTM D 1298	-	0.81 – 0.87
Viscosity at 40 °C	ASTM D 445	cSt	1.8 – 4.1
Pour point	ASTM D 97	°C	Not over 10
Sulphur	ASTM D 2622	%wt.	Not over 0.005
Flash point	ASTM D 93	°C	Not below 52
Distillation, 90% recovered	ASTM D 86	°C	Not over 357

1.1   Cold flow properties of diesel oil

Cold flow properties in cold weather area are a major effect of disruption in engine oil starvation system. This phenomenon was occurred by crystallization of saturated molecules in oil when the oil temperature is reduced below its melting point. Crystallization in oil occurred in two steps known as nucleation and crystal growth. When oil temperature is reduced, heavier saturated molecules in oil solidify to small particle of wax that is nuclei in nucleation step. In continue temperature reduction, nuclei will induce site saturated molecules formation to crystals (solid phase) on its self and expand its size to wax cluster and be separated of liquid oil. Finally, total liquid turns to solid phase at below melting point[3]. The appearance of crystal growth step is shown by turbidity of oil until oil temperature below melting point. In laboratory testing report the temperature for appearance descriptions as follows:

1.1.1 Cloud point (CP)

Cloud point is the temperature of liquid spacemen when the smallest of observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions[4]. This temperature show wax forms a cloudy appearance.

Summary of cloud point testing: The specimen is cooled at a rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the jar test is recorded as a cloud point[4].

1.1.2 Pour point (PP)

Pour point is the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.[5] At this point, the fuel becomes semi solid and lose its flow property, which makes it no pumpable[6]. At this temperature, the appearance of sample spacemen like gel or wax oil.

Summary of pour point testing: after preliminary heating, the sample is cooled at a specified rate and examined at intervals of 1 or 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point[5].
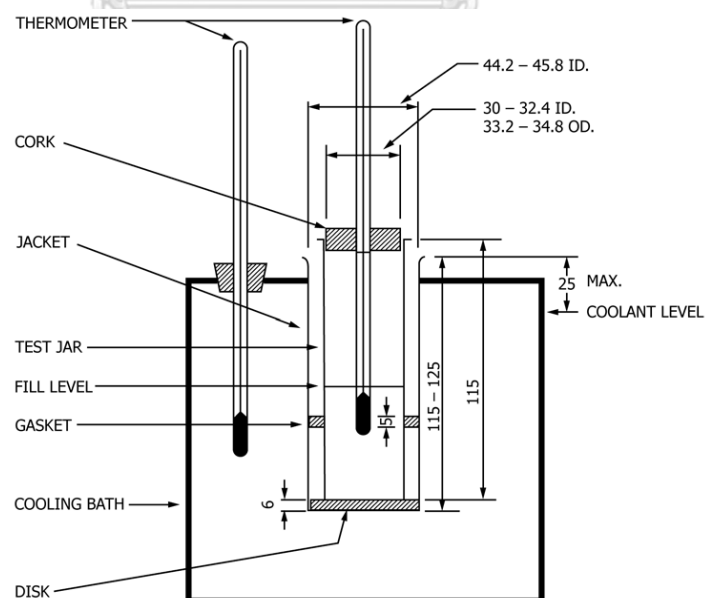
Dimension are in millimeters (not to scale)

Figure 1.1 Apparatus for cloud point and pour point (manual) test

1.1.3 Cold filter plugging point (CFPP)

Cold filter plugging point is the lowest temperature which a given volume of diesel fuel still pass through a standardized filtration device in a specified time when cooled under certain conditions[6]. Summary of cold filter plugging point testing: a specimen of sample is cooled under specified conditions and, at intervals of 1° C, in drawn into a pipe under a controlled vacuum through a standardized wire mesh filter. The procedure is required, as the specimen continues to cool, for each 1°C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipe exceeds 60s or the fuel fails to return completely to the test jar before the fuel has cooled by further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the CFPP[7].
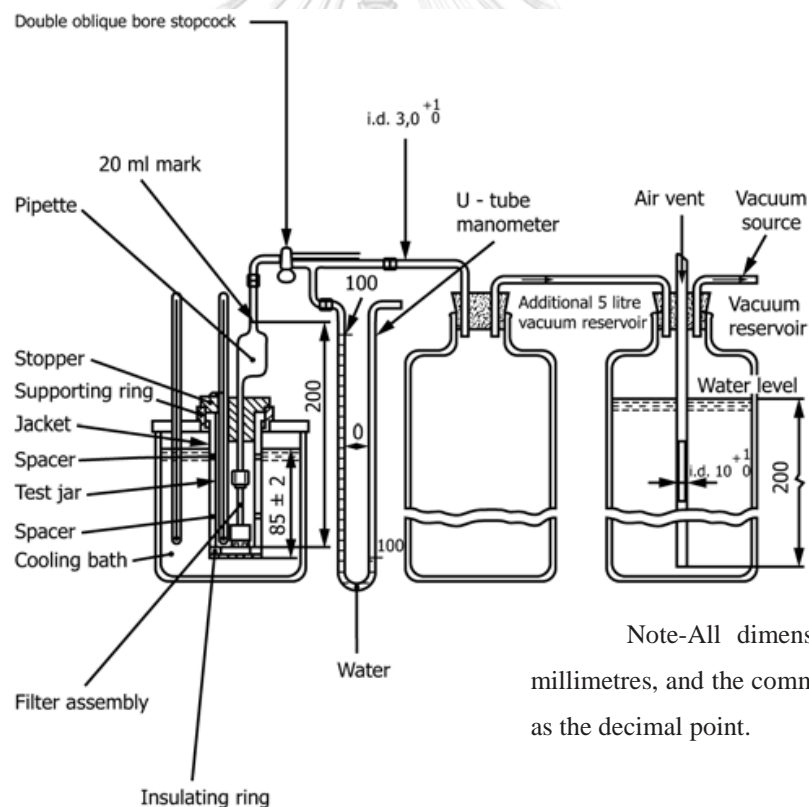
Figure 1.2 Arrangement of manual CFPP apparatus

1.2   The effect of cold flow properties in engine

It is widely known that diesel fuels consist of different molecular weights of hydrocarbon [8]. When diesel is being cooled, as in cold ambient temperatures during winter, the heavier hydrocarbons will typically solidify. This solid will continue to grow and aggregate into lager gelling. These waxes can precipitate out of liquid fuel. This is harmful for fuel filter as the waxes can block the small starving in the engine, thereby plugging the filter. Even if the waxes were to remain suspended in the liquid fuel, if sufficiently large number of such exist due to prolonged exposure to cold weather, their sheer number can still effectively restrict free flow of fuel, hence starving and stalling the engine [9].

1.3   The chemical additives for cold flow properties improvement

The additive technology for cold flow properties improvement firstly developed in crude oil transportation. When waxes deposit on pipe wall, thereby transfer in cold weather. These pipes will stop oil transportation and clean up by scratching equipment and/or high pressure and high temperature technique. If sustainable transportation is required, the addition of some chemicals for deposition inhibition must do in crude oil tank or heating equipment on out site of pipe wall will install before next transport. The chemical is good chance to solve the wax depositions in pipe because that is the preventive solution.

In crude oil transportations, the chemical additive for cold flow properties improvement, as known pour point depressants (PPDs), has been widely researched. The oldest PPD was a chemical which acts as solvent for decreased viscosity such as naphtha, toluene or some oxygenate solvents. In this case the resulting viscosity of the mixture depends on the dilution rate and the respective viscosities and densities of the crude oil and diluents [10-12]. When the mechanism of wax deposition was discovered, PPDs innovation had been developed in many types of chemicals such as fatty acid, modified fatty acid until (co-)polymer [13-15]. The hypothesis of PPDs design was some molecules which can prevent or slowdown of wax agglomerations by changing inhibit or size of crystal interactions when temperature of oil was decreased [16]. PPDs functions can postulate in four mechanisms including nucleation, adsorption, co-

crystallization and improved wax dispersion. These additives result in the formation of smaller wax crystals with more regular shape by any one or combination of above mechanisms [17].

1.3.1 Nucleation

Nucleation is the formation of paraffin crystals in nuclei that are stable in hydrocarbon fluid and which promote crystal growth. Certain PPDs act as nucleation promoters to keep the wax particulate smaller in size to avoid agglomeration. At temperature above wax appearance temperature (WAT), PPDs self-assemble into micelle like aggregates exhibiting crystalline core. Formation of a large number of sub-critical size wax nuclei reduce the growth of one large wax crystal. Wax crystal size reduction makes wax particulates small enough to remain stable in the oil phase mobility [12].

1.3.2 Adsorption

In the crystal growth step, crystal – crystal adhesion in the same direction promotes to bigger wax crystal. But if small wax crystal was adsorbed on the PPD's surface that will inhibit their growth and alter the crystal habits through micelle core formation. That PPD molecules adsorb into the wax crystals and redirect their growth, forming smaller and more isotropic crystals that interfere less with the oil flow. The result of the analysis of various parameters like critical micelle concentration, maximum surface excess and minimum surface area shows that a multilayer, more isotopic and a fixed number of separates from oil phase at a given temperature. Thus, the surface and thermodynamic parameter of the micellization confirms that the suggested mechanism decreases the pour point according to the adsorption behavior of each additive [12].

1.3.3 *Co–crystallization*

This PPD type interferes natural crystallization mechanism in oil by aggregation influence of crystal structure. PPD acts co–crystallization with crystal in oil to wax composition and alters the molecular interactions that helps to prevent the formation of interlocking wax structure. These interactions result in the deformation of the crystal morphology of the crude oil wax. Once it is deformed, these crystals cannot undergo the normal aggregation steps thereby increasing the fluidity [12].

For example, Bharambe, *et al.* (2016) synthesized poly (hexyl oleate–*co*–hexadecyl maleimide–*co*–*n*–alkyl oleate) acts as PPD for flow improvement of Langhnaj crude oil. Nonpolar part of that polymer co–crystallizes with paraffin waxes in crude oil. While polar part blocks network growth leading to decreasing of viscosity. The pour point reducibility of poly (hexyl oleate–*co*–hexadecyl maleimide–*co*–*n*–decyl oleate) and poly (hexyl oleate–*co*–hexadecyl maleimide–*co*–*n*–dodecyl oleate) at 1000 ppm is 6° C. But the effective concentration of that PPD is high. The viscosity of crude oil after blending will significantly change to lower value [18].

Hafiz, *et al*. used hexa-triethanolamine oleate esters as PPD for Umbarkca crude oil. Co–crystallization occurred on oleate chain of PPD and performed micelle to flow improvement by hanging wax in liquid phase of crude oil. The pour point efficiency of hexa – triethanolamine oleate ester at 1000 ppm decrease from 24°C to 12°C for crude oil 1 (ΔPP = 12° C) and from 15° to -3° C (ΔPP = 18° C) for crude oil 2 [14].

In addition, co–crystallization will be a part of complex mechanism of some PPD. Farang, *et al.* 2008 uses poly (cinnamoyl oxy ethyl methacrylate–*co*–octadecyl acrylate) (CEMA–ODA) as PPD for Egyptian waxy crude oils. CEMA–ODA copolymer with molar ratio 1: 3 (CEMA: ODA) is significantly reducing the pour point. For the mechanism, long chain of ODA part brings self–nucleation and induce paraffin in crude oil to co–crystal growth while that wax crystal is adsorbed on CEMA–ODA copolymer. For CEMA part, that incompatible with paraffin, blocks crystal growth and control size of wax. Then wax suspend in crude oil. Decreasing of melting point and pour point of crude oil with CEMA – ODA PPD was observed. The concentration of CEMA – ODA at 5000 ppm significantly decreases pour point from 24° to 6° C (ΔPP = 18 °C) in Karama crude oil [19].

1.3.4 Improved wax dispersion

The presence of PPD improves and alters wax dispersion and also reduce WAT. Its interactions with the soluble wax in the oil due to Van der Waals interactions between paraffin chains and long alkyl moieties. These effects reduce and disperse the amount of precipitated wax and also result in the reduction of WAT. The components in hybrid PPD *co*–crystalize with the paraffin chains and modify the size and shape of wax crystals. In the other hand, the insoluble portion provides heterogeneous nucleation sites for charged wax crystals leading to large electrostatic repulsion, the resultant of which are the slowing down of the formation of the gel networks and enhanced stability of the wax crystals in crude oils [12].

For example, Atta, *et al.* studied effect of additive molecular weight and composition on the flow characteristics of wax crude oil (Norpetco) at low temperature. maleic anhydride ester–*co*–vinyl acetate copolymer additives were prepared with varied monomers feed ratio and different alkyl ester lengths that were dodecyl, stearyl and behenyl alkyl chains. For the best efficiency as PPD even at 5000 ppm was stearyl maleate –vinyl acetate copolymer (VASM) with 1:2 feed ratio ($\Delta PP = 18°C$). The PPD in crude oil changes the wax crystal shapes from extensive interlocking plates to more compact crystals by *co*–crystallization with the wax. The more similar polymer structure to wax components, the better its performance and better its ability to attach to wax components and create a barrier for networking of wax particles. For result extension to image, the microscopic images of Norpetco crude oil without PPD and with VASM 5000 ppm at pour point temperature are shown in Figures 1.3 a and b respectively. For Figure 1.3a, the wax crystal crude oil appeared agglomerated thin and feather–shaped with indicates the growth of wax crystals at nucleating sites. These agglomerates will import high surface energy to crude oil and tend to interconnect into the three–dimension network structure. This interaction increased the pour point of crude oil, And for Figure 1.3b, the addition of 5000 ppm VASM modified the crystal structure to globular morphologies [20].
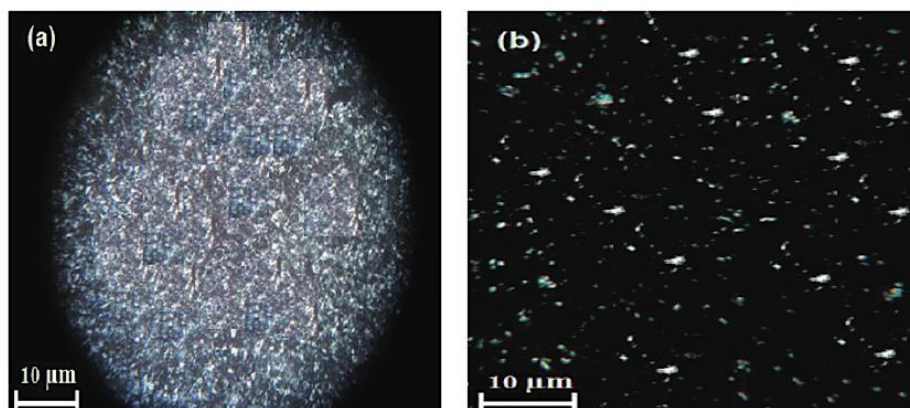
Figure 1.3 Polarized microscopic image morphologies of (a) Norpetco crude oil and (b) Norpetco crude oil with VASM 5000 ppm at their pour point temperature [20].

Al–Sabagh, *et al.* prepared polyester surfactants for PPD in Egyptian Western desert gas oil. Polyethylene glycol–*N,N–bis*(polyethelenyl ethanoic acid) aniline copolymer (CP1) was first interesting copolymer decreased pour point from 18° to 3° C (ΔPP = 15° C). The second polymer was polyethylene glycol–1,3–di(2–oxyethanoic acid) benzene copolymer (CP2) that decreased pour point to 0°C (ΔPP = 18° C). But the most effective pour point decreasing was obtained from CP1+ CP2 blending at ratio 1: 3 of 1000 ppm PPD concentration which decreased pour point to -6° C (ΔPP = 24° C). From the result of photomicrography, at cloud point of gas oil without additive showed large cyclic like crystals (Figure 1.4a) while at cloud point of gas oil with 1000 ppm blending additive showed the broken-down of the cyclic from large wax crystals to fine dispersed wax crystals (Figure 1.4b). That was certainly caused of fluidity gas oil at low temperature [21].
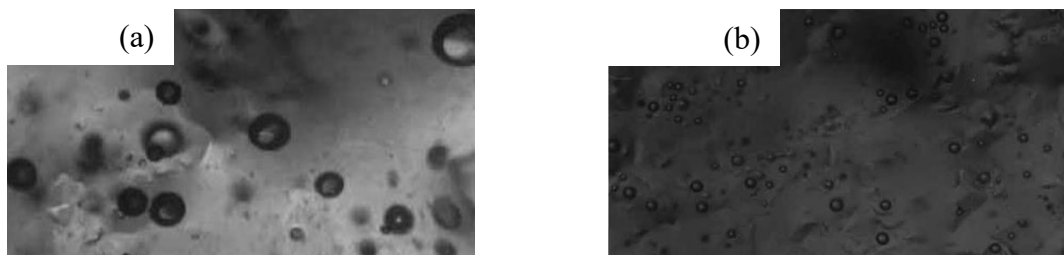
Figure 1.4 Photograph showed wax crystal of (a) origin Egyptian Western desert gas

oil and (b) 1000 ppm of blending additive in Egyptian Western desert

gas oil at cloud point. [21]

1.4 Type of pour point depressants (PPDs)

1.4.1 Copolymers

The physical and chemical properties of PPDs copolymer in solution affects to the performance of cold flow properties improvement. The physical properties of these polymers are based on monomers distribution, whereas the chemical properties are related on the intensive interactions among the molecules, chemical structures and functional groups. The abilities of these types of PPDs are wax crystal interaction and prevention of aggregation process. The flow properties result of wax crude oil after treated by these PPDs type observe in viscosity, rheology, yield stress etc. In addition, the important ability of solution of PPD copolymers is wax solubilization, these PPDs are tested in terms of their suitability in crude oil for flow assurance. The advantages of copolymers are good efficiency in modifying and inhibiting wax depositions. In the other hand, disadvantage is significant the apparent viscosity reducing of crude oil after treating[22-24].

The widely used copolymers are ethylene vinyl acetate, α-olefin maleic anhydride, ethylene butane, 1-docosonal, p-toluene sulfonic acid, etc. with common characteristics and follow mechanism. The α-olefin maleic anhydride is efficient copolymer for wax dispersion in wax crude oil, whereas, ethylene vinyl acetate exhibits a strong influence on the viscosity reduction at an optimum concentration for Brazilian crude oil. Similarly, phthalimide and succinimide copolymers with vinyl acetate,

styrene and methyl methacrylate are investigated for pour point and rheological properties of Egyptian wax crude oil and the result showed that these PPDs satisfy most of the requirements of flow improver[25-28].

1.4.2 Ionic surfactants

Ionic surfactants have been used as PPDs for cold flow improvement in wax crude oils. From identity of surfactants structure, hydrophilic group interacts with paraffin in oil and forms micellization by their wax adsorption in to micelles. Hydrophobic group acts micelles surface repulsion. Wax in micelles cannot be aggregation and disperse in non-wax phase, thereby promotes their pour point improvement. Adding the additives in equal proportion to critical micelle concentration leads to decrease in its tension adsorbed on crystal faces of wax and preventing the crystal growth [29].

For using in crude oil pipeline and in anionic surfactants, the oleophilic end binds to the oil and hydrophilic end binds to water molecule in crude oil and so they are wildly used to improve the pour point by reducing crystals of wax that form caked easily and block the pipeline [23]. For example, calcium o,p-dioctyl benzene sulphonatexide, alkyl benzene sulfonates, and calcium hexyadecyl benzene sulfonate are some of the anionic additives used in wax crude [30].

In case of cationic surfactants usually contained with quaternary amine and carbon side chains. Action of cationic surfactants to pour point improvement similar anionic surfactants. Chloroacetic acid, triethanolamine and vinyl pyridine are some of the cationic chemical additives on wax deposition. Increasing the concentration of the additives leads to an increase in the activity [31]. These surfactant additives show good performance for pour point improvement in waxy crude oil but it expensive than anionic surfactants. Because their high-pressure hydrogenation reaction carried out during synthesis[12].

1.4.3 Non-ionic surfactants

In problem of water containing in crude oil, water was carried to be suspended in oil by micelles of ionic surfactants. Water removing process must be worked load by time and temperature increasing. Then non-ionic surfactants were developed and evaluated to be used as pour point depressants. Different ethoxylated non-ionic surfactants were prepared by reacting natural fatty acids (myristic acid and palmitic acid) with polyethylene glycol of different molecular weight [32]. They do not ionize in aqueous solution due to the presence of hydrophilic groups which are of non-dissociable type such as alcohol, phenol, ether, ester or amide. Non-ionic surfactant acts as wax crystal modifiers, PPDs or flow improvers. They are capable of penetrating into wax crystals and modifying the crystal morphology and growth characteristics thereby reducing the tendency of interconnection to form three-dimensional structure [33]. Some non-ionic surfactants are ethoxylated aliphatic alcohol, poly-oxyethylene surfactants, carboxylic esters, carboxylic amides etc. The ethoxylated non-ionic surfactants are good cloud and pour point depressants for fuel oil.

1.4.4 Nano-hybrid PPD

Nano-hybrid PPDs are composed of polymer matrixes on the surface of inorganic nanoparticles which are prepared by organic modification of nanoclay materials covered by polymeric PPDs like poly-methyl acrylate, ethylene vinyl acetate copolymer, poly-α- olefin, etc [34]. The pour point and apparent viscosity of waxy crude oil decrease significantly with the addition of these nano-hybrid PPDs [28] and their long-term stability is superior to that of conventional PPDs. It also has certain effects on lowering the solidifying point of crude oil. According to the results reported by Majid, et al., nano fluid consists of TiO2:SiO2 (80:20) and 1% polyvinylpyrrolidone which acts as stabilizer and they together prevent the deposition of asphaltene problem. Thus, the nano fluid stabilizes asphaltene particles in crude oil and acts as flow improver in production and surface handling facilities [35].

1.4.5 Bio-based PPD

The bio-based PPD development has received great attention due to their advantages like biodegradability, nontoxicity and reasonable cost. Natural bio-surfactants that contain hydrophilic and hydrophobic (include natural fatty acids) aggregate at interfaces between fluids with different polarities whereby the interfacial surface tension is decreased such as surfactants from soapnut [36]. For interested research, Pseudomonas putida and Halomonas xianhensis that they can be produced bio-surfactants were added or as a mixture to Egypt crude oil. The pour point of that crude oil good reduced. The surface activity of most of the bio-surfactants is maximum at neutral pH. However, the bio-surfactants produced by some organisms are not affected by pH range of 3–12 [37].

In recent studies, synthetic fatty acids esters and vegetable oils have been reported to have positive effects on the pour point reduction in crude oils. The investigation of the use of vegetable oils like jatropha, rubber and castor on flow properties of waxy crude oil has been carried out by Akinyemi et al. (2016) wherein it is found that these vegetable oils are capable of depressing the pour point and viscosity of waxy crude appreciably within a dosage of 0.1–0.3 %v/v. [14].

1.5 Literature review

The polymer based PPDs have been studying in widely copolymer. Initiation using of polymer based PPD were chose from polymer based PPD for crude oil. Such as, Farang et al. (2008)'s research, ethyl methacrylate copolymer was studied as flow improver for Egyptian crude oil. This research was synthesized of cinnamoyloxy ethyl methacrylate (CEMA) monomer and then copolymerization with octadecyl acrylate (ODA) at different molar ratios in the feedstock. The efficiency of these copolymers to depress pour points and rheological characteristics for waxy crude oils using different concentrations of CEMA-ODA additives were studied. CEMA-ODA copolymer with molar ratio 1:3 has good ability to disperse wax crystals and improve the flow behavior of tested crude oils even at temperatures below their pour points [19]. In diesel, copolymer of methyl methacrylate (MMA) was interested as PPD. Soldi, et al. described the synthesis, characterization and performance evaluation of these

copolymers, having as an initial step the synthesis of the alkyl methacrylate monomers by transesterification of methyl methacrylate (MMA) with C14, C16 and C18 fatty alcohols. All the methacrylic copolymers lead to a large reduction in the pour point of samples of Brazilian diesel oil. Oil samples containing 50 ppm of the polymeric additive with 70% octadecyl methacrylate units showed a 22° C reduction in their pour points [38]. From both above researches, pour point depressed mechanism of each sample like co-crystallization. Ester bond act as size-controller of wax crystal in oil. The back-bone of copolymer enhance methacrylate group by steric effect.

In high potential result for pour point improvement of copolymer based PPDs, the problem of exhaust and residue effect in engine were not absolutely obvious. Because there are some researches expanded reduction of pollution emission by polymer-based additive. Such as the studied of Sendilvelan the polymer additive blended in diesel less emitted smoke but other pollution gave the same result of base diesel when exhaust gas for testing were corrected on enhance-combustion of diesel engine [39]. In addition, Hazrat, et al.'s research encouraged polymer additive blended in diesel to reducing pollution emission. The results of 5 % w/v of polymer-type additive in diesel can be reduced CO, NOx when comparisons in base diesel. In summary of this reported, the polymer blended fuels could be potentially used as another emission reducing fuel source in an unmodified diesel engine[emission]. In the other hand, Verma, et al. reported increasing of NOx, CO, CO2 emissions with polymer additive blended diesel. That polymer additive was derived from used tire [40].

Molecular PPDs were developed from natural compound which good act in crude oil. Akinyemi, et al. investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil. Jatropha and castor seed oils depressed the pour point up to about 17° C [13].

Fatty acids were developed to enhancing pour point depression ability. The research of Hafizz, et al., hexa-triethanolamine oleate esters were studied as pour point depressant in two Egyptian waxy crude oil. 1,000 ppm of hexa-triethanolamine monooleate reduced pour point of waxy crude oil A from 24° to 12° C (ΔPP = 12° C) and 1,000 ppm of hexa-triethanolamine trioleate reduced pour point of crude oil B from 15° to -3° C (ΔPP = 18° C). In expansion, waxy crude oil A was high asphaltene act as

natural flow improver, Asphaltenes concentrated on wax crystals and cause the formation of larger slugs, they play the role of bridge between wax. Therefore, the size of wax crystal in crude oil A is in a reduced form. The crystal growth rate of these waxes is slower in crude oil A than crude oil B (less asphaltene, more polar fraction). Then amount of fatty acid (oleate) affected mechanism of crystal growth [14].

Lemos, et al. designed the structures of additive by correlation on effective structure-polymer of pour point depressant. This research identified the effect of four pre-determined chemical groups within the molecules and to set out the best components for maximized inhibition: (i) the length of alkyl chain in the ester group, (ii) the length of the alkyl chain separating the polar nuclei and the ester group, (iii) the heteroatom bonded to the polar nuclei, and (iv) the importance of the naphthoquinone nuclei by calorimetric experiments. The structure of this research liked non-ionic surfactant which containing head (naphthoquinone), linker and tail (ester group). The best result of designed-additive contains naphthoquinone, 2-aminoethane-1-ol and stearic acid that reduced pour point of crude oil 10° C for low density crude oil and 15° C for high density crude oil [41]. This concept is interested for pour point additive in diesel.

In this research designed structure as non-ionic surfactant for pour point additive in diesel. The polar part used glycerol that is by-product from biodiesel process, was modified to solketal and liked to non-polar part with ester bond by esterification. Non-polar part brings from interested fatty acid (stearic acid, palmitic acid, myristic acid, lauric acid, oleic acid and linolenic acid). The effected of polar ability (solketal) on additive was studied in term of pour point reducing ability and comparison with glycerol monoester. Finally, the way to apply the best synthetic pour point additive will be studied by comparison with commercial additive.

1.6 Objective

1. To synthesize and purify synthetic pour point additives from glycerol and selected fatty acids.

2. To study the improvement ability of synthetic pour point additive in petroleum diesel and biodiesel blend.

1.7 Hypothesis

Solketal stearate may be the most effective of pour point reducing ability for diesel because the non-polar part has long chain close component in diesel and polar part can prevent crystal growth of wax in diesel.

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CHAPTER 2

EXPERIMENTAL

2.1   Equipment and instruments

2.1.1   Purification and characterization

For purification step, thin layer chromatography (TLC) was carried on aluminium sheets percoated with silica gel (Merck's, kieselgel 60 PF254). Column chromatography was run on silica gel with pore size 60 °A (Merck grade 7734). The gradient solvent of hexane, dichloromethane (CH_2Cl_2) and ethyl acetate (EtOAc) was used to isolate synthesized compounds. Chemical structures were confirmed by spectroscopy. The ^1H and ^{13}C-NMR spectra were obtained in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference on Varian proton nuclear magnetic resonance spectrometer, model JEOL which operated at 500 MHz. The chemical shifts (δ) are assigned by comparison with $CDCl_3$ solvent proton at 7.26 ppm and the ^{13}C NMR of $CDCl_3$ was at 77.2 ppm.

2.1.2   Diesel properties testing

Important diesel properties were tested by some instrument as follows (Table 2.1) and was assured by verification with certified value of reference material.

Table 2.1 The instruments for diesel properties testing

Instruments	Brand	Model	Reference method
Density meter	Anton Paar	DMA4500	ASTM D 4052-18a [42]
Atmospheric distillation analyzer	PAC	OptiDist	ASTM D 86-20 [43]
Flash point analyzer	HERZOG	HFP-115	ASTM D 93-19 [44]
Pour point analyzer	TANAKA	PMC-102S	ASTM D6749-02 [45]
Viscosity meter	HERZOG	HVM 472	ASTM D445-19 [46]
X-ray fluorescence spectrometer	BRUKER	S8 TIGER	ASTM D4294-16e1 [47]

2.2 Chemicals and reference materials

2.2.1 Reagents for synthesis

The reagents for synthesizing solketal, solketal esters, glyceryl monoester were purchased from Fluka and Merck chemical companies. All solvents used were purified prior to use by standard methodology except for those which were reagent grades.

2.2.2 Reference materials for instrument verification

The reference materials for distillation, flash point, pour point equipment were purchased from PAC company. Density meter was calibrated by kerosene CRM-997970 from STANHOPE-SETA. Viscosity meter was calibrated by CANNON viscosity standard. X-ray fluorescence spectrometer was calibrated standard curve by sulfur in diesel standard from AccuStandard and verified by NIST. All reference materials must have certified value and standard uncertainty. The reference materials were used in instrument preparation step, bring to accuracy results.

2.2.3 Commercial pour point

Commercial additive for the comparison of pour point reducing ability was supplied from Total company in product name: CP 7956 DL (mixture)

2.3 Chemical synthesis

2.3.1 Solketal synthesis [48]

Glycerol and acetone (1:6 mole ratio) were reacted with 1%w/w *p*-toluenesulfonic acid (PTSA) as a catalyst at 60° C for 12 h. Crude products were purified by chromatography. Solketal was characterized by ^{1}H NMR.
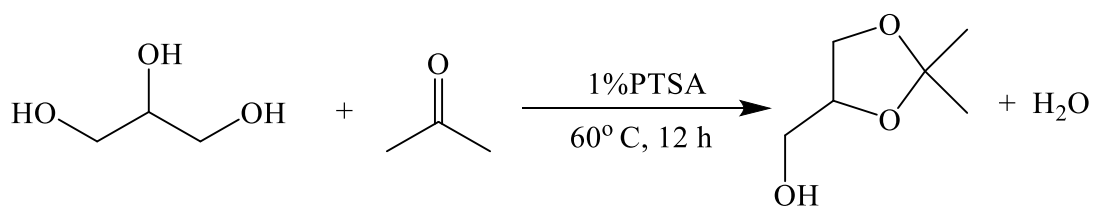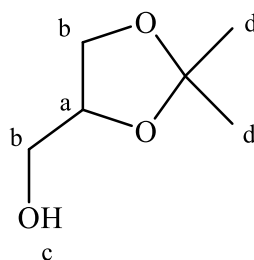
Solketal ^{1}H NMR (CDCl₃) δ (ppm): 4.25 (m, 1H, **CH**), 4.04-3.62 (m, 4H, **CH₂**), 2.59 (s, 1H, **OH**), 1.44 and 1.38 (s, 6H, **CH₃**)

2.3.2 Solketyl esters synthesis

Solketal esters were synthesized by Fischer esterification[49]. Solketal and fatty acid (1.5:1 mole ratio) were reacted with 5%w/w (fatty acid mass) in the presence of catalytic amount of PTSA in no solvent conditions. Temperature that above melting point of fatty acid was set for lauric acid, myristic acid, palmitic acid and stearic acid (Table 2.2). On the other hand, liquid fatty acids were reacted at 60 °C. Total time of this reaction was 4 hours. Crude products were purified by chromatography. Solketal esters were characterized by 1H NMR.
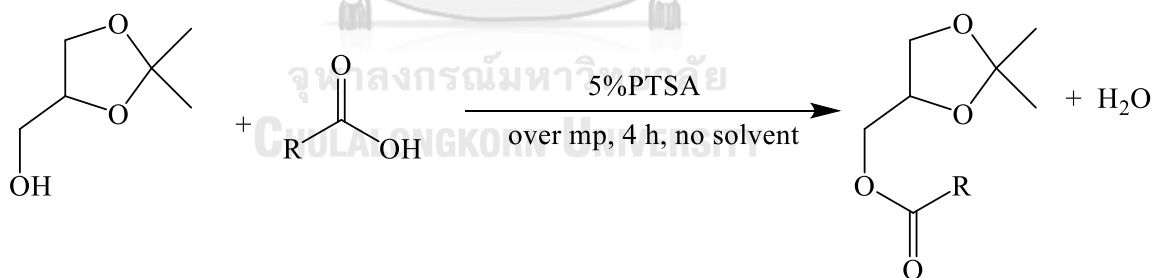
Solketal stearate ^{1}H-NMR (400 MHz) δ (ppm) 4.38–3.53 (m, (**CH₂**)₂**CHO**, 5H), 2.42–2.29 (m, **CH₂**C=O,2H), 1.65 (t, $J = 2.5$ Hz, **CH₂**, 2H), 1.40-1.05 (m, (**CH₂**)₁₃ and (**CH₃**)₂, 32H), 0.97–0.82 (m, **CH₃**, 3H)

Solketal palmitate ^{1}H-NMR (400 MHz) δ (ppm) 5.06–3.52 (m, (**CH₂**)₂**CHO**, 5H), 2.35 (m, **CH₂**C=O, 2H), 1.64 (t, $J = 7.3$ Hz, **CH₂**, 2H), 1.40-1.05 (m, (**CH₂**)₁₂ and (**CH₃**)₂, 30H), 0.89 (t, $J = 6.3$ Hz, **CH₃**, 3H)

Solketal myristate ^{1}H-NMR (400 MHz) δ (ppm) 4.38–3.41 (m, (**CH$_2$**)$_2$**CHO**, 5H), 2.38-2.27 (m, **CH$_2$**C=O, 2H), 1.65 (d, J = 7.4, Hz, **CH$_2$**, 2H), 1.40-1.25 (m, (**CH$_2$**)$_{10}$ and (**CH$_3$**)$_2$, 26H), 0.88 (t, J = 6.6 Hz, **CH$_3$**, 3H)

Solketal laurate ^{1}H-NMR (400 MHz) δ (ppm) 4.38–3.42 (m, (**CH$_2$**)$_2$**CHO**, 5H), 2.34 (td, J = 7.6, 3.1 Hz, **CH$_2$**C=O, 2H), 1.63 (t, J = 7.3 Hz, **CH$_2$**, 2H), 1.44-1.15(m, (**CH$_2$**)$_8$ and (**CH$_3$**)$_2$, 22H), 0.88 (t, J = 6.6 Hz, **CH$_3$**, 3H)

Solketal oleate ^{1}H-NMR (400 MHz) δ (ppm) 5.38 - 5.30 (m,(**CH=CH**), 2H), 4.34 – 4.28 (m, **CH**, 1H), 4.18 – 3.71 (m, (**CH$_2$**)$_2$, 4H), , 2.36 - 2.32 (m, **CH$_2$**C=O, 2H), 2.03 - 1.98 (m, (**CH$_2$**)$_2$, 4H), 1.63 - 1.58 (m, **CH$_2$**, 2H), 1.34 - 1.26 (m, (**CH$_2$**)$_{10}$ and (**CH$_3$**)$_2$, 26H), 0.89 (t, J = 6.72Hz, **CH$_3$**, 3H)

Solketal linoleate ^{1}H-NMR (400 MHz) δ (ppm) 5.49 – 5.24 (m, (**CH=CH**)$_2$, 4H), 4.38 – 4.00 (m, (**CH$_2$**)$_2$, 4H), 3.74 (m, **CH**, 1H), 2.77 (t, J = 6.5 Hz, **CH$_2$**, 2H), 2.35 (t, J = 6.95 Hz, **CH$_2$**CO, 2H), 2.05 (m, (**CH$_2$**)$_2$, 4H), 1.70 – 1.59 (m, **CH$_2$**, 2H), 1.48-1.18 (m,(**CH$_2$**)$_9$ and (**CH$_3$**)$_2$, 24H), 0.89 (t, J = 8.2 Hz, **CH$_3$**, 3H)

Table 2.2 The reaction temperature used for solketyl esters synthesis

Fatty acids	Melting point (°C)	Reaction temperature (°C)
Lauric acid	43.2	60
Myristic acid	54.4	60
Palmitic acid	62.9	70
Stearic acid	69.3	80
Oleic acid	Liquid	60
Linolenic acid	Liquid	60

2.3.3 Glyceryl monoester synthesis

Solketal esters were transformed to monoester glycerin by deprotection of acetone molecule with 4:1 acetic acid/H$_2$O at 50 °C 30 minutes. [50] Crude products were purified by chromatography. Monoester glycerin were characterized by ^{1}H NMR

2.4   Pour point study

2.4.1   Sample preparation

Solketyl esters were prepared at concentrations of 5,000, 3,000, 2,000, 1,000, 500, 300, 200 and 100 mg/kg in base diesel. For well mixing, a sample was warmed at 80□C for 10 min, stirred and observed sample appearance until miscible. Hot sample was cooled down to room temperature before testing. Sample appearance at room temperature was observed.

Commercial pour point additive was prepared in same diesel at the most effectively concentration. For investigation of the most effectively concentration, the maximum differential of pour point between before and after blending with additive was found at the lowest concentration of additive in diesel. The commercial additive concentrations were varied of 50 to 1,000 mg/kg.

For solketal ester effect study, monoester glycerin with the same carbon number of fatty acid part, was prepared at concentration of 5,000, 3,000, 2,000, 1,000, 500, 300, 200 and 100 mg/kg in base diesel.

The mixture of commercial additive and solketal laurate were prepared for pour point testing. The concentration ratio of commercial additive: solketyl laurate were 300:1,000, 300:750, 300:500 and 300:250 mg/kg. Reducing commercial additive concentration to 200 and 100 mg/kg were mixed with solketal laurate at the same above all concentrations.

2.4.2   Pour point analyzer setting and verification

Pour point/Cloud point analyzer TANAKA PMC 102L was set in 1 °C test interval at low pressure program. Analyzer was connected with chiller to control sample block temperature, set temperature at -18 °C. Temperature sensor (PT100) must have calibrated. To confirm the tested results, certify reference material (CRM) pour point value -6 °C was used for verification. Jar test and all sensors were cleaned before testing.

2.4.3 Pour point testing [45]

Pour points of base diesel with and without synthetic additive were measured by pour point analyzer following ASTM D6749. Each sample was measured twice. The difference between two tested results should not be exceeded the repeatability of ASTM D6749 at 1°C test interval.

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CHAPTER 3

RESULTS AND DISCUSSION

3.1   Synthesis and structure characterization

3.1.1   Solketal

From solketal synthesis, the percent yield of solketal was 83 %. The ^{1}H NMR of solketal is presented in figure 3.1
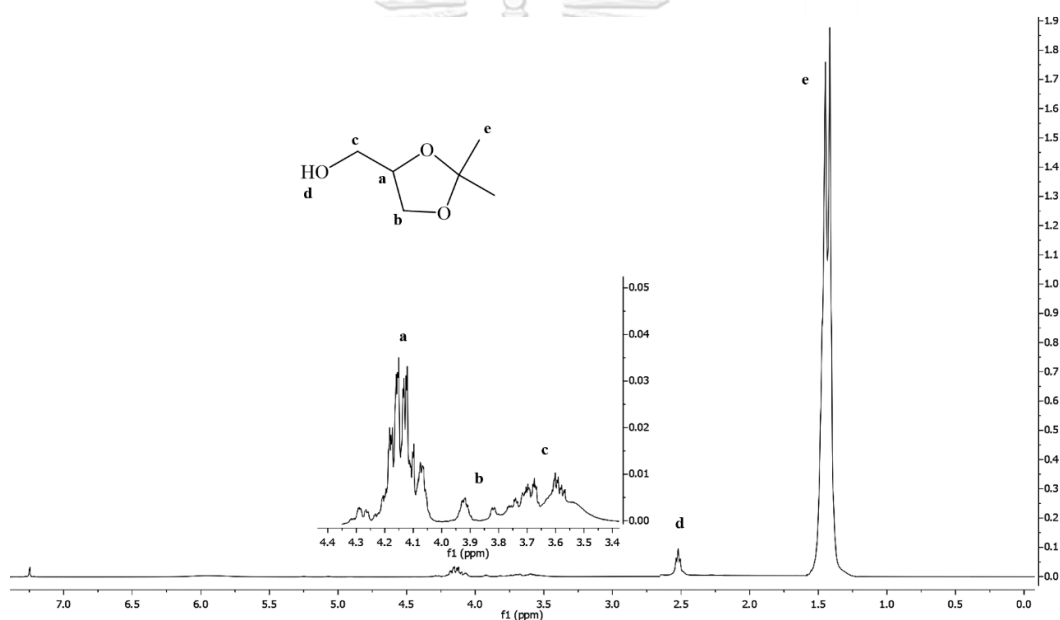
Figure 3.1 ^{1}H NMR spectrum of solketal

The methine proton at position H_a revealed as multiplet peak at δ_H 4.25 ppm (m, $1H_a$). The methylene protons at positions H_b and H_c showed multiplet peak at δ_H 4.00-3.75 ppm (m, $2H_b$) and δ_H 3.75-3.50 ppm (m, $2H_c$), respectively. A hydoxy proton was detected at δ_H 2.59 ppm. Six methyl protons displayed as doublet peak at δ_H 1.40-1.38 ppm (m, $6H_e$)

3.1.2 Solketal ester

Solketal esters were synthesized by esterification of solketal and selected fatty acids (stearic acid, palmitic acid, myristic acid, lauric acid, oleic acid and linolenic acid). The percentage yield of solketal stearate was 93%, 91% for solketal palmitate, 87% for solketal myristate, 87% for solketal laurate, 73% for solketal oleate and 67% for solketal linolinate. The ^{1}H NMR spectra are shown in Figures 3.2-3.7.
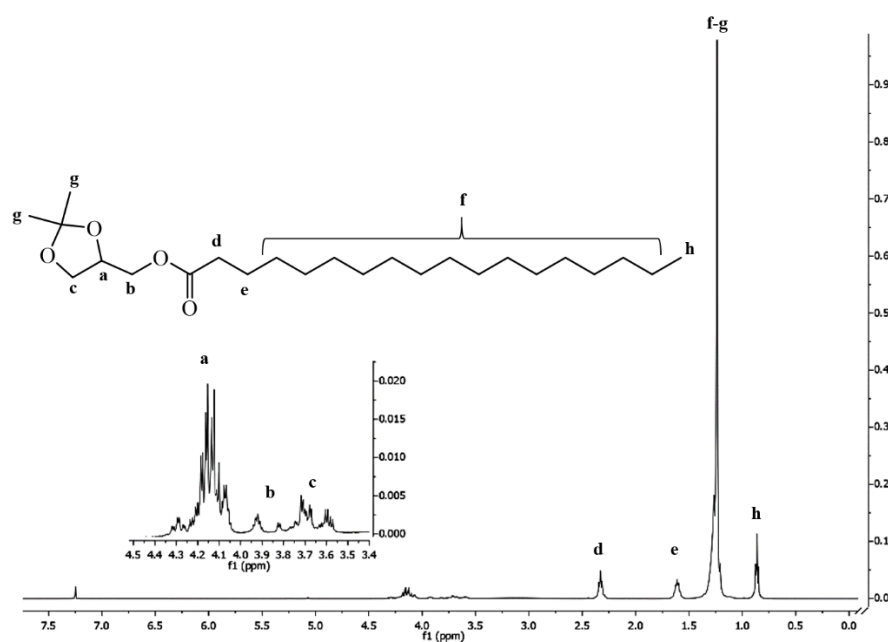
Figure 3.2 ^{1}H NMR spectrum of solketal stearate

The methine proton at position H_a revealed multiplet peak at δ_H 4.25 ppm (m, $1H_a$). The methylene protons at positions H_b and H_c showed multiplet peak at δ_H 4.00-3.80 ppm (m, $2H_b$) and δ_H 3.75-3.55 ppm (m, $2H_c$), respectively. The methylene proton beside carbonyl group revealed a triplet peak at δ_H 2.42 ppm (t, $2H_d$). The next methylene proton exposed as a multiplet peak at δ_H 1.65 ppm (m, $2H_e$). At δ_H 1.40-1.05 ppm were the multiple signals of 26 methylene protons ($26H_f$) and 6 methyl protons ($6H_g$). Three methyl protons showed multiplet peak at δ_H 0.87 ppm (m, $3H_h$). The solketal stearate is white solid.
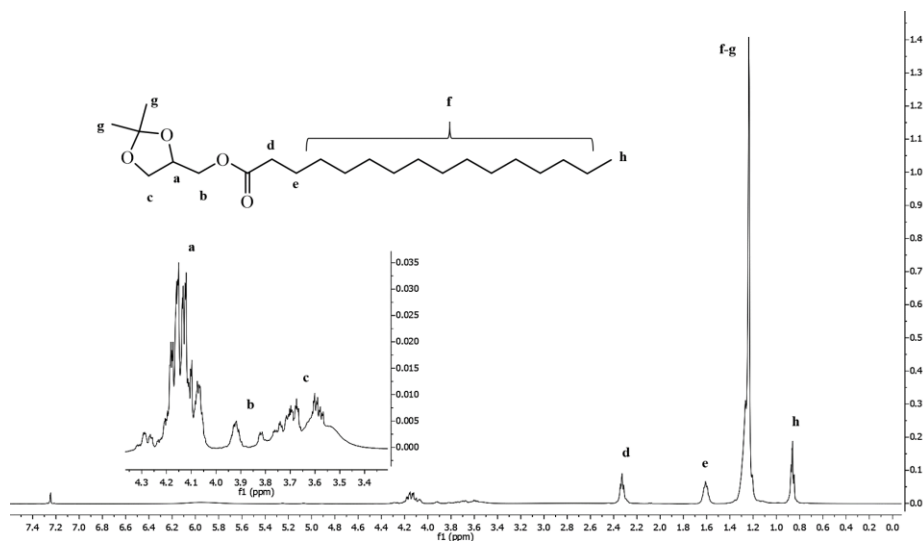
Figure 3.3 ^{1}H NMR spectrum of solketal palmitate

The methine proton at position H_a revealed a multiplet peak at δ_H 4.14 ppm (*m*, 1H_a). The methylene protons at positions H_b and H_c showed multiplet peak at δ_H 3.96-3.79 ppm (m, 2H_b) and δ_H 3.78-3.54 ppm (m, 2H_c), respectively. The methylene proton beside carbonyl group revealed as a triplet peak at δ_H 2.33 ppm (t, 2H_d). The methylene proton exposed as a multiplet peak at δ_H 1.66 ppm (m, 2H_e). At δ_H 1.40-1.13 ppm, multiple signals of 24 methylene protons (22H_f) and 6 methyl protons (6H_g). Three methyl protons showed multiplet peak at δ_H 0.86 ppm (m, 3H_i). The solketal palmitate is white solid.
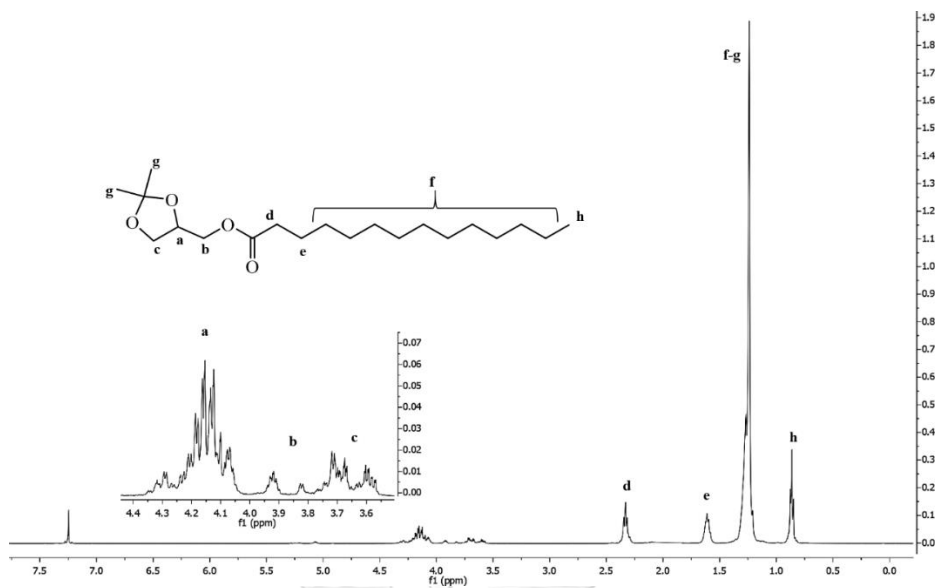
Figure 3.4 ^{1}H NMR spectrum of solketal myristate in CDCl$_3$

The methine proton at position H$_a$ revealed multiplet peak at δ_H 4.16 ppm (m, 1H$_a$). The methylene protons at positions H$_b$ and H$_c$ showed multiplet peak at δ_H 3.95-3.84 ppm (m, 2H$_b$) and δ_H 3.85-3.53 ppm (m, 2H$_c$), respectively. The methylene proton beside carbonyl group revealed triplet peak at δ_H 2.33 ppm (t, 2H$_d$). For next methylene proton exposed multiplet peak at δ_H 1.61 ppm (m, 2H$_e$). At δ_H 1.40-1.25 ppm were multiple signals of 20 methylene protons (20H$_f$) and 6 methyl protons (6H$_g$). Three methyl protons showed multiplet peak at δ_H 0.87 ppm (m, 3H$_h$). The solketal myristate is white solid.
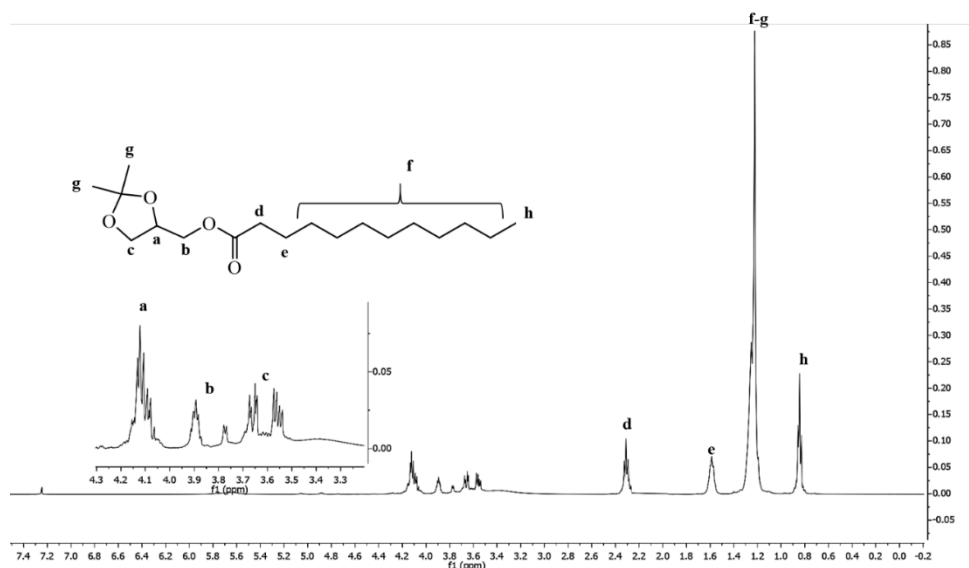
Figure 3.5 ^{1}H NMR spectrum of solketal laurate in CDCl$_3$

At δ_H 4.12 ppm was multiplet signal of methine proton of a proton H$_a$. The methylene protons at positions H$_b$ and H$_c$ showed multiplet peak at δ_H 3.95-3.75 ppm (m, 2H$_b$) and δ_H 3.75-3.50 ppm (m, 2H$_c$), respectively. The triplet peak at δ_H 2.31 ppm (t, 2H$_d$) was the sign of two methylene protons at position H$_d$. H$_e$ was exposed as a multiplet peak of two methylene protons. The multiplet signals at δ_H 1.40-1.15 ppm were multiple signals of 16 methylene protons (16H$_f$) and 6 methyl protons (6H$_g$). At δ_H 0.85 ppm showed multiplet peak of 3 methyl protons (m, 3H$_i$). The solketal laurate is white solid.
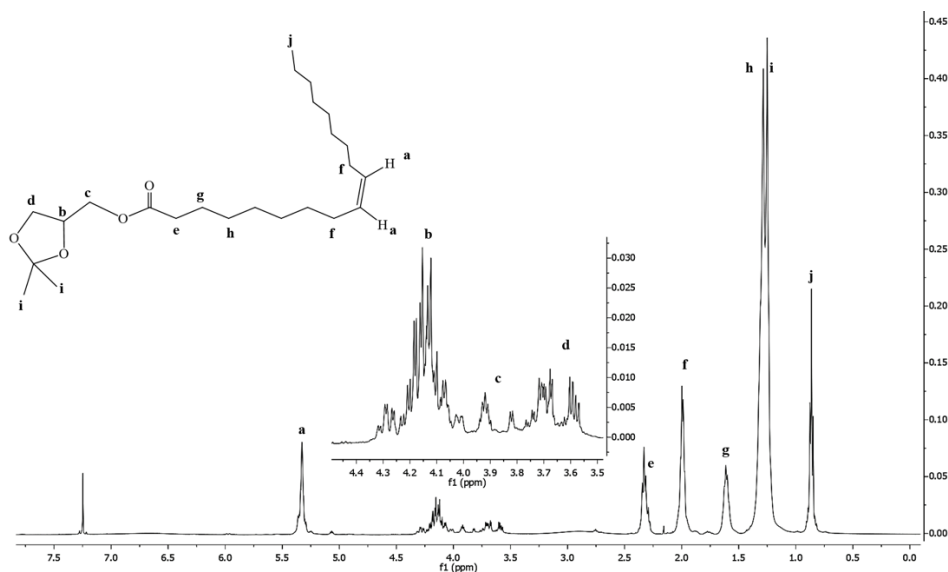
Figure 3.6 ^{1}H NMR spectrum of solketal oleate in CDCl$_3$

Two olefinic protons revealed as multiplet peak at δ_H 5.33 ppm (*m*, 2H$_a$). H$_b$ and four methylene protons of H$_c$ and H$_d$ revealed as multiplet peak at δ_H 4.35-4.00 ppm (m, H$_b$) and δ_H 3.75-3.55 ppm (m, 4H$_{c,d}$), respectively. The methylene protons beside a carbonyl group revealed as multiplet peak at δ_H 2.32 ppm (m, 2H$_e$). Four methylene protons of H$_f$ nearly double bond exposed as multiplet peak at δ_H 1.99 ppm (m, 4H$_f$). H$_g$ showed as multiplet peak at δ_H 1.29 ppm (m, 20H$_g$). At δ_H 1.25 ppm was multiplet signals of 6 methyl protons (6H$_h$). Three methyl protons signaled as multiplet peak at δ_H 0.86 ppm (m, 3H$_i$). The solketal oleate is light yellow liquid.
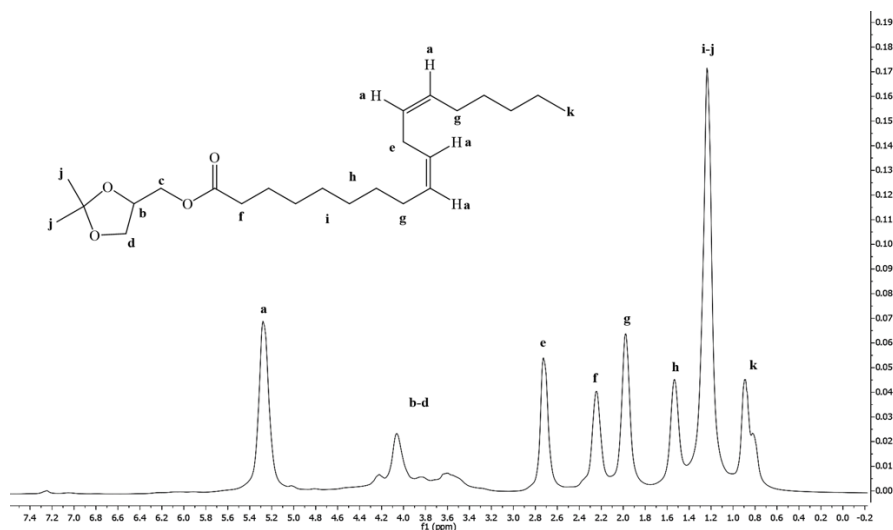
Figure 3.7 ^{1}H NMR spructrum of solketal linolinate in CDCl$_3$

The olefinic protons of H$_a$ revealed at δ_H 5.29 ppm (*m*, 4H$_a$). At δ_H 4.40-3.35 ppm could be assigned for the signal of methine proton of H$_b$ and four methylene protons of H$_c$ and H$_d$. H$_e$ was the midst methylene proton of double bond appeared at δ_H 2.73 ppm (2H$_e$). The signal at δ_H 2.24 (2H$_f$) ppm was the signal of methylene protons. The methylene protons at δ_H 1.98 ppm could be assigned for 2H$_g$. Next methylene protons exposed as multiplet peak at δ_H 1.53 ppm (m, 2H$_h$). At δ_H 1.43-1.03 ppm were multiplet signals of 14 methylene protons (14H$_i$) and 6 methyl protons (6H$_j$). The signal of terminal methyl protons could be observed at δ_H 0.87 ppm (m, 3H$_k$). The solketal linoleate is brown liquid.

3.1.3 Monoester glycerin

The best performance of synthetic additives for pour point was solketal laurate. The deacetonization of solketal laurate yielded glycerol monolaurate or monolaurin as clear and viscos liquid. The ^{1}H NMR spectrum of glyceryl monolaurate is shown in Figure 3.7.

Figure 3.8 ^{1}H NMR spructrum of glycerol monolaurate in CDCl$_3$

The hydroxy proton at position H$_a$ showed the quinet peak at δ_H 4.88 ppm (quin, 2H$_a$). All protons of glycerol showed three groups of δ_H 3.93-3.53 ppm, H$_b$ at δ_H 3.93-3.75 ppm (pp, 2H$_b$), H$_c$ as doublet of doublet peak at δ_H 3.79-3.76 ppm and H$_d$ at δ_H 3.69-3.53 ppm (dd, 2H$_d$). The triplet peak at δ_H 2.32 ppm was methylene proton beside the carbonyl group of H$_e$. The methylene proton at H$_f$ showed multiplet peak at δ_H 1.59 ppm (m, 2H$_f$). The methylene protons of alkyl chain gave multiplet signals at δ_H 1.24 ppm (16H$_g$). At δ_H 0.85 ppm was triplet peak of terminal methyl protons (t, 3H$_h$). The glycerol monolaurate is clearly viscous liquid.

3.2   Pour point study

3.2.1   Appearance

Diesel for engine must be bright and clear. Thus, the appearance of prepared solketal esters in diesel at room temperature (22° C) was first tested. The results are presented in Table 3.1.

Table 3.1 Appearance of diesel with solketal ester additives at room temperature (22° C)

Additive	Concentration (mg/kg)							
	5,000	3,000	2,000	1,000	500	300	200	100
Solketal stearate	Hazy	Hazy	Hazy	Hazy	Clear	Clear	Clear	Clear
Solketal palmitate	Hazy	Hazy	Hazy	Hazy	Clear	Clear	Clear	Clear
Solketal myristate	Hazy	Hazy	Hazy	Hazy	Clear	Clear	Clear	Clear
Solketal laurate	Hazy	Hazy	Hazy	Hazy	Clear	Clear	Clear	Clear
Solketal oleate	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Solketal linoleate	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear

The results in red box revealed that the synthetic additives were undissolvable in diesel and hazy oil occurred. The results in green box on the other hand clearly displayed that the synthetic additives could dissolve in diesel and clear oil was obtained. It should be noted that with the addition of solid solketal ester additives at the concentration of 1,000 mg/kg and more, the blended diesels were hazy oil at room temperature (22° C). Nonetheless, all could be miscible at 30° C. This can be explained that solid additives at high concentrations (more than 1,000 mg/kg) in diesel might be self-aggregation of long chain hydrocarbon. At the concentration lower than 1,000 mg/kg, blended diesels were clear at room temperature. For liquid additives, the bright and clear diesels were observed at every concentration.

3.2.2 Pour point of diesel containing solketal ester

The results of pour point of diesel blened with solketal esters are presented in Figure 3.9.
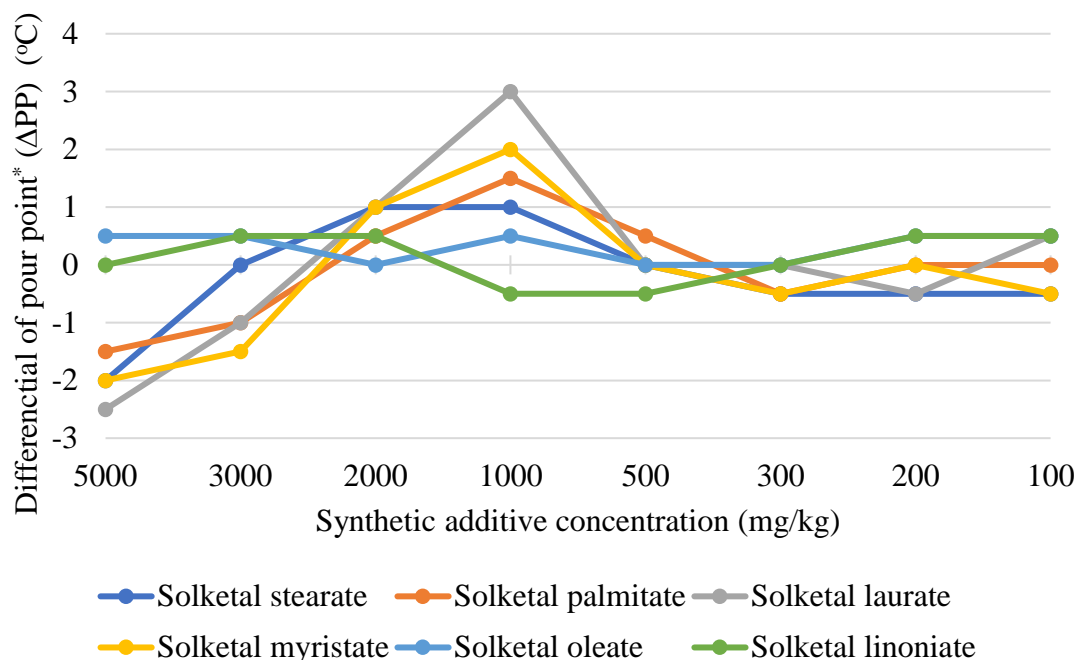
*Differential of pour point is the result of pour point of base diesel minus pour point of diesel with synthetic additive.

Figure 3.9 The pour point of diesel blened with solketal esters

at various concentrations

Differential of pour point was used to explain the effectiveness of synthetic additives. Zero-degree Celsius results mean no changing of pour point. The positive (+) and negative (-) signs indicated pour point decreasing and increasing, respectively.

Solid solketal esters (solketal laurate, solketal myristate, solketal palmitate and solketal stearate) could reduce pour point of base diesel at concentrations of 1,000–2,000 mg/kg. This could describe that long chain fatty acid may interact with paraffin component and solketal part could prevent crystal growth in their wax diesel. At higher concentration (> 2,000 mg/kg), those solketal esters increased pour point of diesel because total saturated hydrocarbon was over optimum concentration. In addition, with the concentrations of soketal ester (all cases) lower than 1,000 mg/kg, they could not reduce pour point. This was probably because interaction between the long chain fatty

acid and paraffin in diesel was too low and solketal part could not prevent crystal growth. Solketal laurate (gray line) at 1,000 mg/kg was the best pour point additive with maximum reduced pour point of base diesel (ΔPP = 3°C). Liquid solketal esters (solketal oleate and solketal linoleate) did not significantly alter pour point of diesel.

3.2.3 Pour point of diesel containing commercial additive

The pour point of commercial additive (CP 7956 DL) is shown in Figure 3.10.
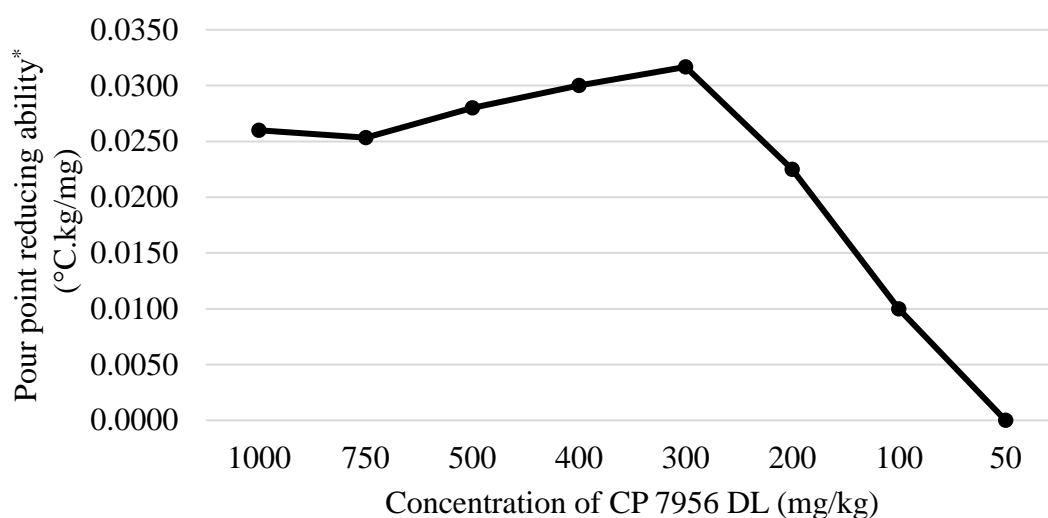
*Pour point reducing ability was calculated by dividing different of pour points on base diesel and diesel with commercial additive by concentration of commercial additive.

Figure 3.10 The pour point reducing ability of diesel containing commercial additive

The lowest concentration of commercial additive that provided the maximum pour point reducing ability was defined in terms of pour point reduction of 1 mg/kg commercial additive. Concentration of CP 7956 DL of 300 mg/kg was the optimum for reducing 10 □C of pour point of diesel. This concentration was selected as a benchmark to compare with synthetic additives. It was found that the commercial additive revealed better pour point reducing ability than synthetic additives. Even solketal laurate which was the best synthetic additive still needed higher doses in diesel than commercial additive.

3.2.4 Pour point of diesel with the mixed solketal ester and commercial additive

Despite unsatisfied pour points results of synthetic additive, this part aims to explore the possibility of the utilization of solketal laurate. It was disclosed that solketal laurate could be used as pour point additive by blending with commercial additive. The pour point results of solketal laurate and commercial additive are shown in terms of differential pour point between base diesel and diesel mixed with commercial additive (Figure 3.11).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Comm. (mg/kg)	300	200	200	200	200	200	200	100	100	100	100	100	100	0
Syn. (mg/kg)	0	1000	750	500	250	100	0	1000	750	500	250	100	0	1000
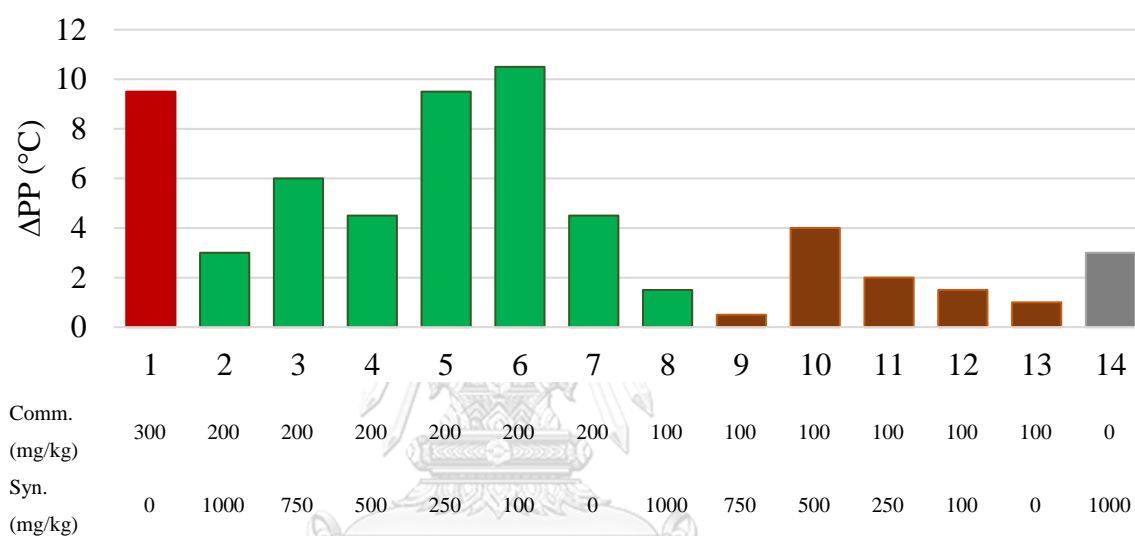
Figure 3.11 The differential pour point of 300 mg/kg commercial additive (red), the result of differential pour point of additive mixed on diesel (green: fixed commercial concentration at 200 mg/kg, brown: fixed commercial concentration at 100 mg/kg), the differential pour point of 1,000 mg/kg solketal laurate (gray).

The mixture of 200 mg/kg commercial additive and 100 mg/kg solketal laurate gave amazing results that could reduce 10.5° C of pour point. This result displayed better pour point reducing ability of diesel blended with 300 mg/kg commercial additive (the best concentration). This clearly demonstrated that synthetic solketal laurate enhanced pour point reducing ability of commercial additive. The pour point reducing mechanism of solketal laurate and commercial additive was interesting to further study.

3.2.5 Pour point of monoester glycerin

To confirm solketal effect, glycerol monolaurate was studied and the results are presented in Figure 3.12.
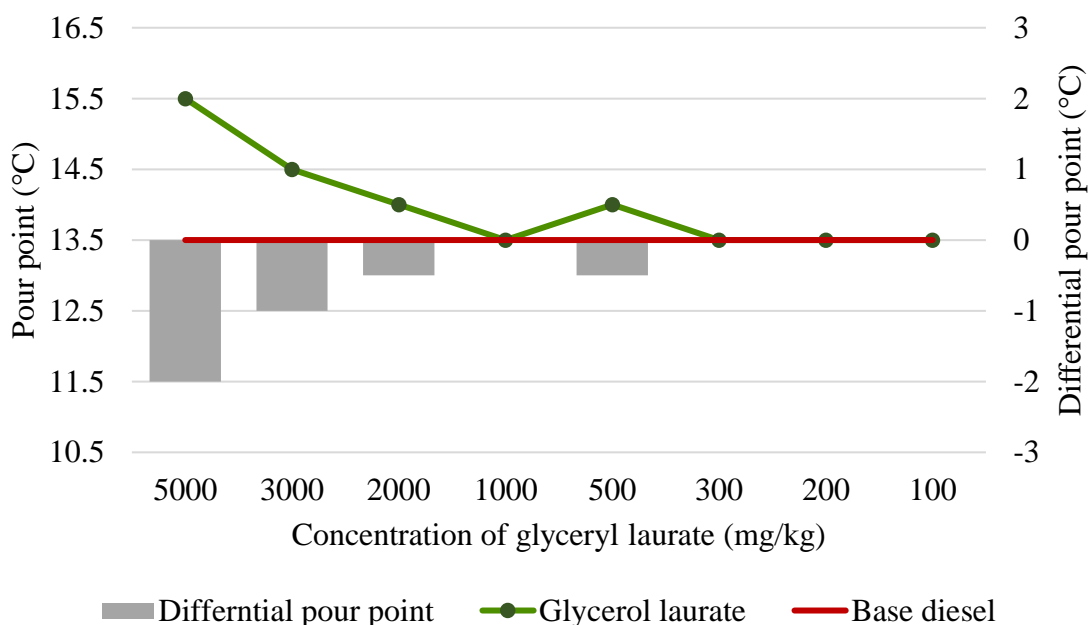
Figure 3.12 The pour point result of diesel with glycerol laurate (green) compared with pour point of base diesel (red) and differential pour point of diesel

with glycerol laurate (gray)

Glycerol monolaurate could not significantly reduce pour point on diesel at all testing concentrations. To describe this, the hydroxyl group of glycerol could not crystal growth blocking. Although hydroxyl group has higher polar than solketal but that maybe too small for block or depress crystal growth of paraffin in diesel. Hydroxy group of solketal ester bind together with hydrogen bonding which had higher interaction than Van der Waal's interaction between paraffin in diesel and laurate group. While the solketal structure has more steric effect, paraffin molecules in diesel difficultly interacted together.

3.2.6 The properties of diesel

After the best synthetic additive for pour point improvement was found, the critical properties of diesel after blending must test for confirmation following commercial specification. Table 3.2 shows the properties of all studied diesel.

Table 3.2 The result of diesel properties

Item	Unit	Result				Benchmark
		A	B	C	D	
Appearance		B&C	Hazy	B&C	B&C	B&C
API	-	37.8	37.7	37.8	37.8	31.1 – 43.2
Density at 15 °C	g/cm^3	0.8354	0.8359	0.8354	0.8354	-
SG 15.6/15.6 °C		0.8358	0.8358	0.8358	0.8358	0.81 – 0.87
Viscosity at 40 °C	cSt	3.005	3.006	2.988	2.996	1.8 – 4.1
Pour point	°C	14	11	4	3	10 MAX
Sulphur	%w/w	42.0	41.8	42.0	42.0	0.005 MAX
Flash point	°C	70	70	70	70	52 MIN
Distillation,						
50% recovered	°C	277.4	277.2	277.6	277.4	-
90% recovered	°C	356.2	356.5	356.8	356.6	357 MAX

Note: A: Base diesel without additive, B: Blended base diesel with 1,000 mg/kg of solketal laurate, C: Blended base diesel with 300 mg/kg of commercial additive D: Blended base diesel with additive mixed (200 mg/kg of commercial and 100 mg/kg of solketal laurate), B&C: Bright and Clear, SG: Specific gravity

Overall test items did not significantly change except appearance and pour point. Although pour point reduced lower base diesel but appearance of diesel blended with 1,000 mg/kg was hazy and pour point reduced ability was lower than commercial additive. Only solketal laurate could absolutely not be used as pour point additive. Nevertheless, the mixture of solketal laurate and commercial additive showed the high pour point reduced ability with clear blended diesel. In addition, overall properties of blended diesel with mixed additive gave acceptable results compared with commercial high-speed diesel benchmark.

CHAPTER 4

CONCLUSION

The main objective of this study is to increase value of glycerol in petroleum industry. Glycerol was transformed to solketal. Synthetic additives were synthesized from solketal and selected fatty acids. The cold flow properties improvement of the diesel with those synthetic additives were studied in terms of pour point of diesel.

The solketal was synthesized by glycerol esterification with 1%w/w *p*-toluenesulfonic acid (PTSA) as a catalyst at 60°C for 12 h. Furthermore, solketal esters were synthesized by Fischer esterification. Solketal and fatty acid (1.5:1 mole ratio) were reacted with 5%w/w (fatty acid mass) in the presence of catalytic amount of PTSA in no solvent conditions. For pour point reducing ability on diesel were defined by 1. comparison pour point of blended diesel with solketal ester and non-blened additive, 2. comparison pour point of blended diesel with solketal ester and commercial additive and 3. effect of solketal in solketal ester on pour point reducing ability of diesel.

The 1,000 mg/kg of solketal laurate gave the highest pour point reducing ability of base diesel (ΔPP = 3 °C) and the solketal inhibited crystal growth of paffins in diesel. But the appearance of blended diesel with 1,000 mk/kg of solketal laurate was hazy. That could not be used as pour point additive in commercial diesel because blended diesel was not usable.

Although, the pour point reducing ability of solketal esters were lower than that of commercial additive. Solketal laurate was discovered to be able to use as additive in diesel by blending with commercial additive at certain ratio. Mixed-additive could reduce nore pour point of diesel than using only commercial additive in diesel. In addition, one third of import commercial additive could be substituted by solketal laurate that caused of capital cost reduction.

The propose for the future work, glycerol has been interesting for fuel additives because glycerol was cheap and mass by-product. Glycerol will be reacted with other ketones such as 3-pentanone, 5-nonanone, 7-tridecanone, *etc.* for studying as pour point additives. The structures of (2,2-dialkyl-1,3-dioxolan-4-yl)methanol are like non-ionic surfactants. Pour point reducing ability and other purpose should also be studied on blended diesel.

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APPENDIX

Appendix I The pour point result of synthetic additives in base diesel

Synthetic additive	Concentration (mg/kg)	Pour point (°C)			S^*	ΔPP^{**}	r^{***} evaluation
		1	2	average			
None additive	0	14	13	13.5	0.71	1	PASS
Solketal stearate	5000	16	15	15.5	0.71	1	PASS
	3000	14	13	13.5	0.71	1	PASS
	2000	12	13	12.5	0.71	1	PASS
	1000	12	13	12.5	0.71	1	PASS
	500	13	14	13.5	0.71	1	PASS
	300	14	14	14	0.00	0	PASS
	200	14	14	14	0.00	0	PASS
	100	14	14	14	0.00	0	PASS
Solketal palmitate	5000	15	15	15	0.00	0	PASS
	3000	14	15	14.5	0.71	1	PASS
	2000	13	13	13	0.00	0	PASS
	1000	12	12	12	0.00	0	PASS
	500	13	13	13	0.00	0	PASS
	300	14	14	14	0.00	0	PASS
	200	13	14	13.5	0.71	1	PASS
	100	14	13	13.5	0.71	1	PASS
Solketal myristiate	5000	16	15	15.5	0.71	1	PASS
	3000	15	15	15	0.00	0	PASS
	2000	13	12	12.5	0.71	1	PASS
	1000	11	11	11	0.00	0	PASS
	500	14	13	13.5	0.71	1	PASS
	300	14	14	14	0.00	0	PASS
	200	14	13	13.5	0.71	1	PASS
	100	14	14	14	0.00	0	PASS

Appendix I The pour point result of synthetic additives in base diesel (continue)

Synthetic additive	Concentration (mg/kg)	Pour point (°C)			S^*	ΔPP^{**}	r^{***} evaluation
		1	2	average			
Solketal laurate	0	14	13	13.5	0.71	1	PASS
	2000	13	12	12.5	0.71	1	PASS
	1000	11	10	10.5	0.71	1	PASS
	500	14	13	13.5	0.71	1	PASS
	300	13	14	13.5	0.71	1	PASS
	200	14	14	14	0.00	0	PASS
	100	13	13	13	0.00	0	PASS
Solketal oleate	5000	13	13	13	0.00	0	PASS
	3000	13	13	13	0.00	0	PASS
	2000	14	13	13.5	0.71	1	PASS
	1000	13	13	13	0.00	0	PASS
	500	13	14	13.5	0.71	1	PASS
	300	13	14	13.5	0.71	1	PASS
	200	13	13	13	0.00	0	PASS
	100	13	13	13	0.00	0	PASS
Solketal linoniate	5000	13	14	13.5	0.71	1	PASS
	3000	13	13	13	0.00	0	PASS
	2000	13	13	13	0.00	0	PASS
	1000	14	14	14	0.00	0	PASS
	500	14	14	14	0.00	0	PASS
	300	13	14	13.5	0.71	1	PASS
	200	13	13	13	0.00	0	PASS
	100	13	13	13	0.00	0	PASS

*S: Standard deviation = $\sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n-1}}$, $^{**}\Delta PP$: Difference of two pour point result =

$|x_1 - x_2|$ thereby x_1 = first measured pour point result and x_2 = second measured pour

point result, ***r: repeatability of pour point result. The difference of two results must do not over 1.1 °C as followed ASTM D6749. Thereby PASS means ΔPP≤1.1 °C

Appendix II The pour point result of commercial additives in base diesel

Concentration of CP 7956 DL (mg/kg)	Pour point (°C)			ΔPP (°C)	ΔPP/Conc. (°C.kg/mg)
	1	2	Average		
1000	-12	-13	-12.5	26	0.0260
750	-6	-5	-5.5	19	0.0253
500	-1	0	-0.5	14	0.0280
400	2	1	1.5	12	0.0300
300	4	4	4	9.5	0.0317
200	9	9	9	4.5	0.0225
100	12	13	12.5	1	0.0100
50	13	14	13.5	0	0.0000
0	14	13	13.5	0	-

ΔPP = pour point of base diesel minus pour point of diesel with commercial additive

Appendix III The pour point result of glycerol monolaurate in base diesel

Concentration of glycerol monolaurate (mg/kg)	Pourpoint (°C)			ΔPP (°C)
	1	2	average	
5000	16	15	15.5	-2
3000	15	14	14.5	-1
2000	14	14	14	-0.5
1000	14	13	13.5	0
500	14	14	14	-0.5
300	13	14	13.5	0
200	14	13	13.5	0
100	13	14	13.5	0

ΔPP = pour point of base diesel minus pour point of diesel with commercial additive

Appendix IV The pour point result of additive mixed in base diesel

Concentration of additive (mg/kg)		Pour point (°C)			ΔPP
Commercial	Solketal laurate	1	2	average	(°C)
300	0	4	4	4	9.5
200	1000	10	11	10.5	3
200	750	8	7	7.5	6
200	500	9	9	9	4.5
200	250	4	4	4	9.5
200	100	3	3	3	10.5
200	0	9	9	9	4.5
100	1000	12	12	12	1.5
100	750	13	13	13	0.5
100	500	10	9	9.5	4
100	250	11	12	11.5	2
100	100	12	12	12	1.5
100	0	12	13	12.5	1
0	1000	11	10	10.5	3
0	0	14	13	13.5	-

ΔPP = pour point of base diesel minus pour point of diesel with additive mixed

Appendix V Test result of base diesel (without additive)

Item	Method	Result		
		1	**2**	**average**
Appearance	Visual	Bright & Clear		
API		37.8	37.8	37.8
Density at 15 °C (g/cm^3)	ASTM D4052-12	0.8354	0.8354	0.8354
SG at 15.6 °C/15.6 °C		0.8358	0.8358	0.8358
Viscosity at 40 °C (cSt)	ASTM D445-17a	3.004	3.006	3.005
Pour point (°C)	ASTM D4629	14	13	14[*]
Sulphur (mg/kg)	ASTM D2622-10	42.0	42.0	42.0
Flash point (°C)	ASTM D93-16a	71	70	70
Distillation, (°C)				
50% recovered	ASTM D86-17	277.3	277.5	277.4
90% recovered		356.2	356.1	356.2

[*]Out of specification (10 °C maximum)

Note: Pour point and flash point report in no decimal form followed ASTM D4629 and ASTM D 93-16a respectively

Appendix VI Test result of base diesel with 1,000 mg/kg of solketal laurate

Item	Method	Result		
		1	2	average
Appearance	Visual	Hazy[*]		
API		37.7	37.7	37.7
Density at 15 °C (g/cm^3)	ASTM D4052-12	0.8359	0.8359	0.8359
SG at 15.6 °C/15.6 °C		0.8363	0.8363	0.8358
Viscosity at 40 °C (cSt)	ASTM D445-17a	3.007	3.006	3.006
Pour point (°C)	ASTM D4629	11	10	11[**]
Sulphur (mg/kg)	ASTM D2622-10	41.8	41.9	41.8
Flash point (°C)	ASTM D93-16a	71	70	70
Distillation, (°C)				
50% recovered	ASTM D86-17	277.1	277.3	277.2
90% recovered		356.4	356.6	356.5

[*]Not to use

[**]Out of specification (10 °C maximum)

Note: Pour point and flash point report in no decimal form followed ASTM D4629 and ASTM D 93-16a respectively

Appendix VII Test result of base diesel with 300 mg/kg of commercial additive

Item	Method	Result		
		1	**2**	**average**
Appearance	Visual	Bright & Clear		
API		37.8	37.8	37.8
Density at 15 °C (g/cm^3)	ASTM D4052-12	0.8354	0.8354	0.8354
SG at 15.6 °C/15.6 °C		0.8358	0.8358	0.8358
Viscosity at 40 °C (cSt)	ASTM D445-17a	2.987	2.988	2.988
Pour point (°C)	ASTM D4629	4	4	4
Sulphur (mg/kg)	ASTM D2622-10	41.9	42.0	42.0
Flash point (°C)	ASTM D93-16a	70	70	70
Distillation, (°C)				
50% recovered	ASTM D86-17	277.5	277.7	277.6
90% recovered		356.8	356.9	356.8

Note: Pour point and flash point report in no decimal form followed ASTM D4629 and ASTM D 93-16a respectively

Appendix VIII Test result of base diesel with additive mixed

(200 mg.kg of commercial additive and 100 mg/kg of solketal laurate)

Item	Method	Result		
		1	**2**	**average**
Appearance	Visual	Bright & Clear		
API		37.8	37.8	37.8
Density at 15 °C (g/cm^3)	ASTM D4052-12	0.8354	0.8354	0.8354
SG at 15.6 °C/15.6 °C		0.8358	0.8358	0.8358
Viscosity at 40 °C (cSt)	ASTM D445-17a	2.995	2.997	2.996
Pour point (°C)	ASTM D4629	3	3	3
Sulphur (mg/kg)	ASTM D2622-10	42.0	42.1	42.0
Flash point (°C)	ASTM D93-16a	70	70	70
Distillation, (°C)				
50% recovered	ASTM D86-17	277.3	277.5	277.4
90% recovered		356.6	356.6	356.6

Note: Pour point and flash point report in no decimal form followed ASTM D4629 and ASTM D 93-16a respectively

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