

## BLENDS OF LAURATE ESTER WITH MENTHOL AND CAMPHOR AS SYNTHETIC BASE FLUID

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### Abstract

The preferred base fluids for formulating synthetic-based mud (SBM) for drilling problematic and sensitive oil and gas wells are usually of mineral oils origin. However, the toxic, non-biodegradable and non-renewable properties of these oils increase the cost of treating drilled cuttings prior to their discharge. This has necessitated a diversion of research interests to alternative synthetic base fluids, of which ester is one. In this work, the potential of isopropyl laurate and its blends as synthetic base fluids for oil well drilling mud formulation was investigated. The density, kinematic viscosity and flash point of the neat ester and the blends were compared with that of commercially available mineral base fluid, and API recommended values. The results obtained indicated that the additives led to an increase in the viscosity and density of the samples while lowering the flash point. Change in physical properties observed from the addition of menthol, however, was less than that from camphor. These values, however, are still within the acceptable API range for ester base fluids, the ester and its blends, therefore, possess suitable physicochemical properties appropriate for the synthetic base fluid application.

**Keywords:** ester; additives; flash point; density; menthol; camphor; base fluid.

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## 1. Introduction

The petroleum industry utilizes a large amount of drilling mud for maximization of offshore and onshore oil and gas drilling operations [1]. Oil based mud has always been preferable in drilling operations because of their better technical performance relative to water-based drilling muds, especially when drilling through sensitive shale formations, and in the drilling of extended and deviated wells [2]. Their toxic, non-biodegradable nature, however, made them unable to meet the strict cuttings discharge requirements for aquatic environment [3-4]. Thus drill cuttings from a well drilled with mineral oil or diesel based fluid must be processed to reduce the percentage of residual base fluid to an acceptable level before disposal into aquatic ecosystems; a process that increases the overall drilling cost [5-7]. Synthetic base fluid (SBF) is a relatively new player when it comes to the formulation of oil and gas well drilling muds [8], and was introduced as a result of the search for base fluids that will combine the better technical properties of mineral oil base fluid with eco-friendliness [9-10]. Esters, together with poly alpha olefins (PAOs), internal olefins (IOs) and linear alpha olefins (LAOs) are the four major categories of SBFs that have been applied with success over the years. Esters have proved to be the most biodegradable of them all and has been employed in the drilling of several hundreds of wells since their introduction. A lot of research efforts, therefore, have been expended in the search for suitable synthetic ester base fluids, a quest that led to the investigation of natural oils like soybean and groundnut oil, biodiesel from palm and coconut oils, and esters from esterification of free fatty acids for their suitability as synthetic base fluid for drilling mud with encouraging levels of success achieved [2,8,11-13]. Working with a free fatty acid has the advantage of yielding a cleaner ester with well-defined structure instead of a cocktail of fatty acid esters as obtainable from transesterification of fats and oils.

The properties of interest for base fluid employed in formulating drilling muds for oil and gas wells include flash point, density, kinematic viscosity, thermal and hydrolytic stability, and elastomer compatibility. Ideally, an ester base fluid should have high flash point, low pour point, low viscosity, high thermal and hydrolytic stability and be compatible with existing elastomer [3]. It has been established from the literature that these physicochemical properties of esters are influenced by blending with additives like polystyrene and waste plastics [14-15]. The United States Patent Nos. 8,414,717 and 9,932,533 disclosed a method that improves the flash point of volatile organic solvents including esters and petroleum products, by blending with  $\alpha$ -terpineol [16-17].

Camphor is a white or transparent waxy solid obtained from the essential oil distilled out of the fragrant camphor tree (*Cinnamomum camphora*, L.) and other trees from the laurel family such as basil, rosemary and sage [18-19], while menthol is a naturally occurring monoterpene found in mint plants like menthol mint (*Mentha arvensis*, L.), spearmint and peppermint (*Mentha piperita*, L.) [20-21]. These terpenoids have a long history of being used as perfumes, medicines and spices [22-23], their utilization as blends in esters, however, is a relatively unexplored area of research.

The aim of this research therefore, is to investigate the effect of blending isopropyl laurate with menthol and camphor on the physical properties of isopropyl laurate and determine the suitability of the ester and the blends as synthetic base fluid for oil drilling mud by comparing these parameters with that of a commercial base mineral fluid which serves as reference.

## 2. Materials and methods

The reference base fluid utilized in this study was supplied by SNEP Co. Lauric acid was esterified with isopropyl alcohol over the sulphamic acid catalyst at a temperature of 120°C for three hours according to the method reported by Orji *et al.* [12]. The Fourier Transform infra-red (FTIR) spectra of lauric acid, isopropyl alcohol, and isopropyl laurate were obtained on a Shimadzu FTIR 8400S spectrophotometer, in the range of 4000-600  $\text{cm}^{-1}$ .

Three different blends of isopropyl ester each for menthol and camphor were prepared with 5, 10, and 15% of the additives. The kinematic viscosities of the neat ester, the blends, and the reference fluid at 40°C and 100°C were determined according to ASTM D445 method; the flash point was evaluated using Pensky-Martens closed cup method (ASTM D93) and the density determined according to ASTM D1298. Each of the samples was run in triplicates, and the average values rounded to the nearest whole number as reported.

## 3. Results and discussion

### 3.1. FTIR spectroscopic analysis of the synthesized ester

The IR spectrum of isopropyl laurate was compared with that of standards in order to assign the absorption peaks to the respective functional groups. The characteristic absorption peaks of the ester functional group were observed at 1111 and 1180  $\text{cm}^{-1}$  (C-O), 1720  $\text{cm}^{-1}$  (C=O), and 2924  $\text{cm}^{-1}$  (CH). The spectrum of isopropyl laurate was also compared with the spectra of lauric acid and isopropanol. The absence of the absorption peak of the OH functional group of isopropanol and the movement of the absorbance for lauric acid carbonyl (1720  $\text{cm}^{-1}$ ) toward shorter wavelength (1697  $\text{cm}^{-1}$ ) indicate that the synthesis of isopropyl laurate was achieved. These results are summarized in Table 1, while the spectra are shown in Figures 1 through 3.

Table 1. Absorption peaks in the IR spectra of isopropyl laurate, isopropanol, and lauric acid

S/No	Functional group	Wave number ( $\text{cm}^{-1}$ )		
		Isopropyl laurate	Isopropanol	Lauric acid
1	C=O	1720	-	1697
2	C-O	1180	1126	1026
		1111		1080
3	CH <sub>2</sub>	2924	2970	2916
4	C-H	1373	1311	1350
		1350	1381	1419
			1411	
5	O-H	-	3340	-

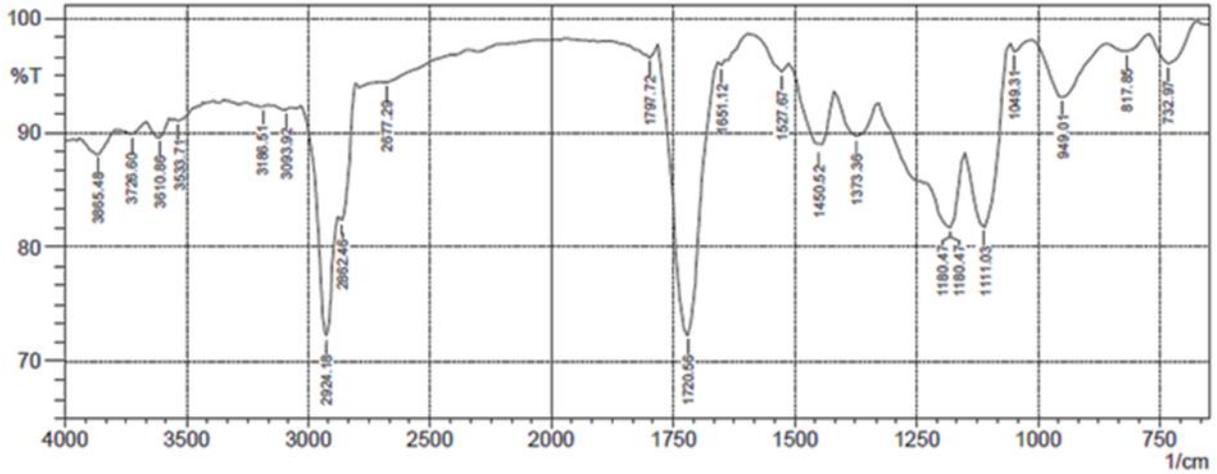


Figure 1. FTIR spectrum of isopropyl laurate (IL)

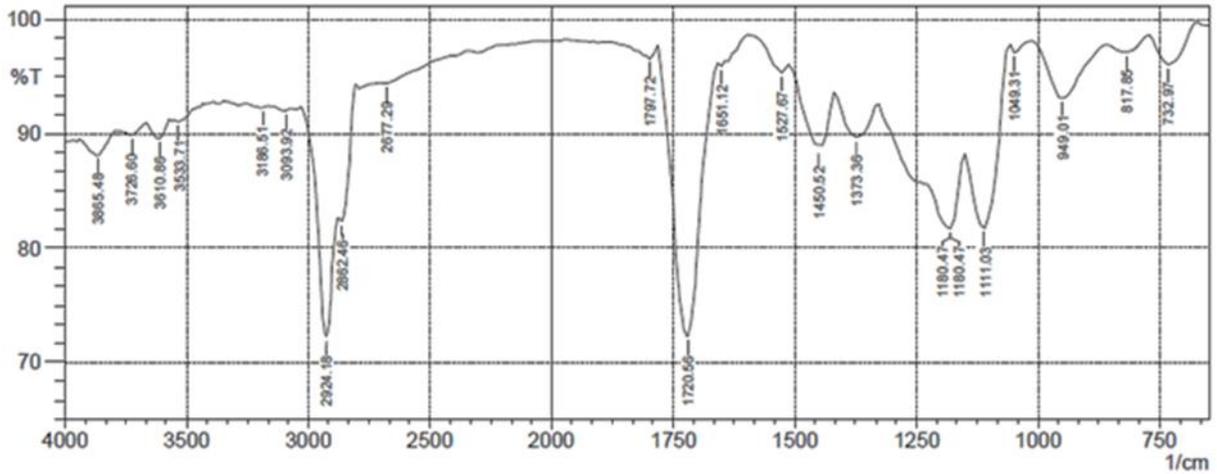


Figure 2. FTIR spectrum of lauric acid

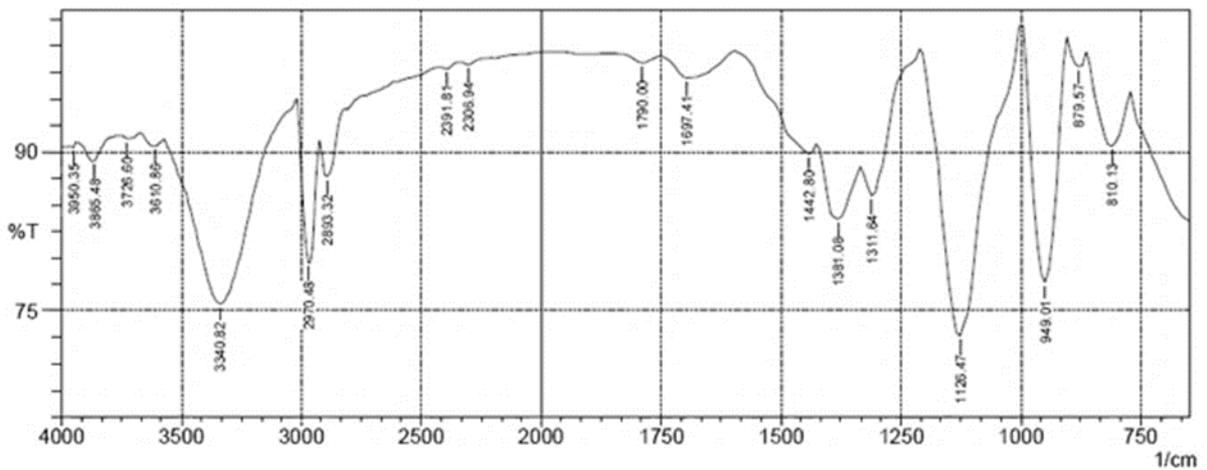


Figure 3. FTIR spectrum of isopropanol

### 3.2. Physical properties of the base fluids

The flash point of the reference fluid and the ester with its blends are presented in Figure 1. The flash point of a fluid is the minimum temperature at which it can generate enough ignitable vapour in the air close to its surface. A liquid with a higher flash point is relatively more difficult to ignite and therefore is safer to handle at a higher temperature. Thus, a drilling mud formulated with a base fluid with a high flash point will pose less fire hazard since less ignitable vapour is expected to accumulate above the mud. It has been suggested that the flash point of a base fluid for drilling mud application should exceed 100°C [24]. The result of the flash point determination for isopropyl laurate, its blends, and the reference indicates that the unblended isopropyl laurate has the highest flash point (118°C) whereas the blended isopropyl laurate with 20 % menthol has the lowest flash point (104°C). The isopropyl laurate with 10 % menthol exhibited a better flash point compared to the one with 15 % and 20 % menthol. The flash point of the IL and its menthol blends, however, are higher than that of the reference (103°C). Addition of camphor to IL led to a higher degree of reduction in the flash point. At 10 % addition of camphor, the flash point went as low as 61°C. The subsequent increase in the percentage of camphor; however, improved the flash point to 65°C (15%) and 79 °C (20%). The reduction in flash point on blending with additives could be attributed to the volatile nature of menthol and camphor.

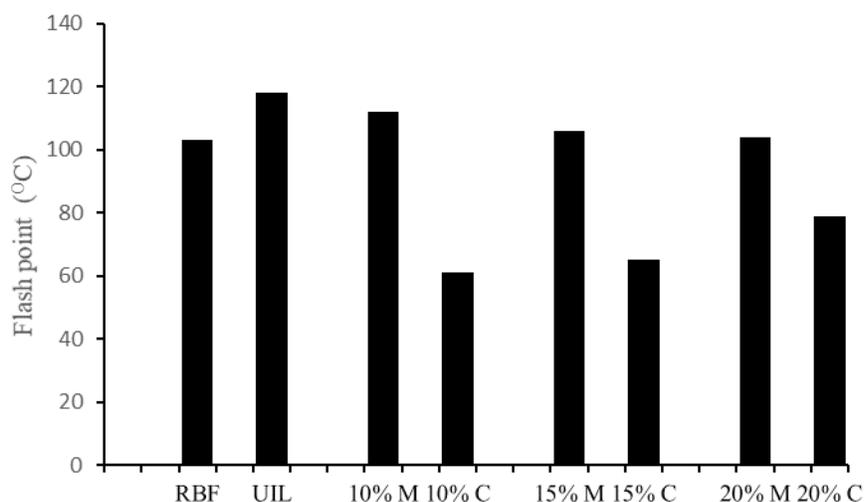


Figure 4. Flash point of isopropyl laurate and its blends

Rheological and hydraulic properties of drilling mud are affected by the kinematic viscosity of the base fluid from which it was formulated. Hence, a viscous base fluid tends to produce a viscous drilling mud which because of its poor pump-ability is more problematic to manage relative to low viscosity muds. Moreover, low viscosity base fluids when utilized in formulating drilling muds, exhibit better tolerance towards the presence of solids and water in the final formulation and increases the quantity of brine used, thereby reducing cost [25-26]. The effect of different percentage of additives on kinematic viscosity of the isopropyl ester samples at 40°C and 100°C are presented in Figure 5.

The result obtained from measuring the kinematic viscosity of the various blends indicates that inclusion of the additives led to an increase in viscosity at both temperatures. However, the highest viscosity values of 4.37 cSt at 100°C and 1.68 cSt at 40°C were recorded at 10 % menthol and 10% camphor respectively. The subsequent increase in the concentration of either additive resulted in a decrease in viscosity values. The ester and its blends recorded higher viscosity values at both temperatures relative to the reference; this is to be expected since the reference fluid is a synthetic hydrocarbon base fluid. It has been suggested that base fluid for drilling mud formulation should have viscosity values ranging from 1 to 6 cSt at 40°C [27].

Thus, the viscosity values of the ester and its blends are within acceptable values for base fluid application.

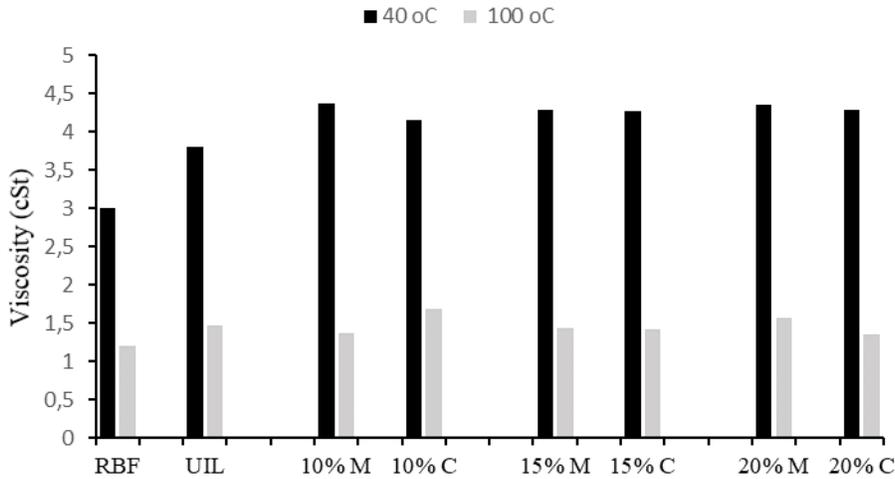


Figure 5. Kinematic viscosity of isopropyl laurate and its blends at 40°C and 100°C

The density of a base fluid affects the quantity of material required to achieve a particular standard of mud weight while formulating mud. It is required that the density of an oil base fluid be less than that of water which is 1 g/cm<sup>3</sup>. From the result of the density determination presented in Figure 6, the RBF has the lowest value of 0.81 g/cm<sup>3</sup>, followed by the unblended ester with 0.84 g/cm<sup>3</sup>. It was observed that blending with menthol and camphor led to a slight increase in density. Thus the density of the ester with 10 and 15 % camphor is 0.86 g/cm<sup>3</sup>. Increasing the percentage of camphor to 20 moved the density from 0.86 to 0.87 g/cm<sup>3</sup>. Addition of menthol also did not bring about a significant increase in the density of the ester. The values range from 0.85, 0.85 and 0.86 g/cm<sup>3</sup> for 10, 15, and 20 % menthol respectively. These results are all within the recommended values for synthetic base fluid since they are all lower than the density of water.

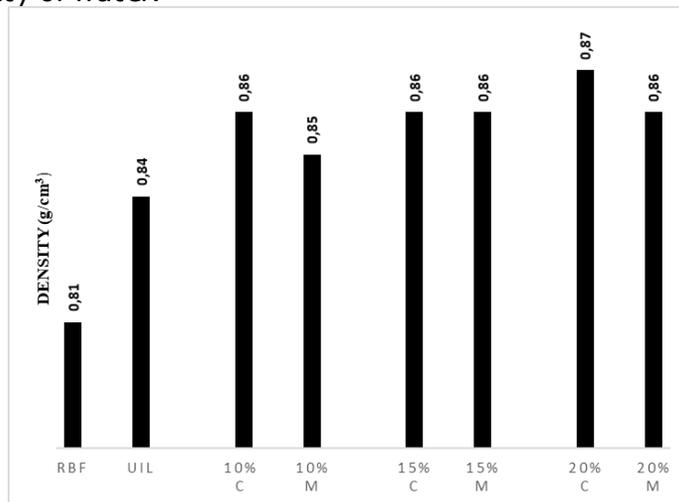


Figure 6. Density of isopropyl laurate and its blends at room temperature

#### 4. Conclusion

From the results obtained in this work, it can be concluded that isopropyl laurate was successfully synthesized as determined proved by FTIR analysis. Isopropyl laurate has a higher flash point than the RBF.

Blending IL with camphor and menthol reduced the flash point of the ester and increased the viscosity and density marginally.

These results have demonstrated that isopropyl laurate and its blends possess properties which make them suitable for the base fluid application. It is recommended that the menthol ester blends they should be used in the formulation of inverse emulsion drilling muds for low-temperature shallow wells to avoid fire hazards since they recorded the lowest flash points of all the samples analyzed.

### List of symbols

RBF	Reference base fluid
IL	Isopropyl laurate
UIL	Unblended isopropyl laurate
10%M	Ester blended with 10% menthol
10%C	Ester blended with 10% camphor
15%M	Ester blended with 15% menthol
15%C	Ester blended with 15% camphor
20%M	Ester blended with 20% menthol
20%C	Ester blended with 20% camphor
cSt	Centistoke

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