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STARCH FATTY ESTERS FOR POTENTIAL USE IN PETROLEUM INDUSTRY

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Abstract. The aim of this study was to obtain and characterize starch fatty esters with variations in the hydrophilic/lipophilic balance and to assess whether these samples have potential application in oil-based drilling fluids. The variation in the hydrophobicity of the samples was verified by means of viscosity tests, which suggested that the products had varied solubility parameters, near the value of the solvent n-paraffin.

Keywords: modified starch, fatty acid esters, transesterification, n-paraffin, drill fluid.

1. Introduction

Products made from starch have attracted the interest of researchers and companies due to the abundance of starch in nature, its low cost and biodegradability [1, 2]. Modified starches are widely used for many purposes, from biodegradable packaging material to components of oil-drilling mud [2, 3]. Besides these applications in the oil industry, starch compounds can act to reduce filtrate, modify rheological properties, stabilize shales and reduce drag, as well as they can be used in advanced oil recovery (EOR) processes [4, 5]. The influx of the liquid phase, known as filtrate, in productive zones can cause a significant reduction of permeability and hence lower well productivity [6,7]. The incorporation of natural gums and starch-based materials in drilling fluids compositions was the primary solution to control this phenomenon [8]. The absence of reports of the modified starches use in non-aqueous drilling fluid formulations motivates research in this area.

The main methods used to introduce hydrophobic groups in the polysaccharide chain are based on esterification reactions of starch with acids chloride in

the presence of organic solvents, such as pyridine, toluene, dimethylacetamide and dimethylformamide [9-11]. Because of the toxicity of these reagents, esterification reactions starting from mixtures of anhydrates and transesterification in the presence of methyl and vinyl fatty acids have been re-investigated and adapted [12-20]. Other acylation agents, such as carboxyamides, ketenes and peroxides can also be employed to obtain starch esters [11]. The major difficulty in obtaining highly substituted derivatives is the dissolution of granular starch in an appropriate medium without causing significant degradation [14, 17-18, 20-21]. According to Muljana and collaborators [20], vinyl esters are more reactive than methyl esters and anhydrides because of these reagents leaving group properties. Acylation of starch with vinyl esters occurs through an addition-elimination mechanism, with the formation of acetaldehyde as a gaseous byproduct, which favors the shift in the equilibrium of the reaction toward formation of the desired product [14].

The main objective of this work was to synthesize and characterize starch fatty esters with potential application as additives in paraffin-based drilling fluids. These materials were also evaluated regarding their thermal resistance and rheological behavior in the presence of the solvent n-paraffin, to note the variations of the samples solubility parameters.

2. Experimental

2.1. Materials

Gelatinized cornstarch and the solvent n-paraffin were donated by Poland Quimica Ltda. (Duque de Caxias, RJ). The reagents vinyl stearate and vinyl laurate (synthesis grade) were obtained from Sigma-Aldrich

Brasil Ltda. (São Paulo, SP). The dried dimethyl sulfoxide P.A. solvent and the anhydrous catalyst potassium carbonate P.A. (synthesis grade) were purchased from Vetec Química Fina Ltda. (Rio de Janeiro, RJ). Deuterated dimethyl sulfoxide (DMSO- d_6) and deuterated chloroform ($CDCl_3$) solvents were supplied by Sigma-Aldrich Brasil Ltda. (São Paulo, SP).

2.2. Synthesis of the Starch Fatty Esters

The starch was modified chemically by transesterification reaction with vinyl laurate (C-12) or vinyl stearate (C-18), in the presence of a basic catalyst. The starch modification reaction was carried out in dimethyl sulfoxide (DMSO) at 383 K for 24 h under an inert atmosphere (N_2) [16, 17]. Six structural types, coded as SVS-01, SVS-02, SVS-03, SVL-01, SVL-02 and SVL-03 were synthesized. The initials SVS and SVL refer to the materials obtained from vinyl stearate and vinyl laurate, respectively. The indexes 01, 02 and 03 are related to the vinyl ester/starch molar ratios of 1:1, 2:1 and 3:1, respectively. The acetaldehyde gas byproduct was removed from the system by absorption in an alkaline solution with the aid of a bubbler. The products were recovered and purified, using the commercial methanol, and dried in an oven at 343 K. The choice of the starch/vinyl ester/DMSO reaction system was based on the simplicity of the process of purifying the products and the high conversion rates.

2.3. Characterization of the Chemically Modified Starches

2.3.1. Fourier transform infrared (FTIR) spectroscopy

The absorption spectra in the infrared region of the samples were obtained with a Varian Excalibur 3100 FTIR spectrometer (Varian Inc., Palo Alto, CA, USA) equipped with the ATR accessory and zinc selenide crystal. A total of 100 scans were performed in the region from 4000 to 400 cm^{-1} , with resolution of 4 cm^{-1} .

2.3.2. Hydrogen nuclear magnetic resonance (1H NMR) spectrometry

The nuclear magnetic resonance (1H NMR) spectra of the esterified products were obtained in a Varian Mercury VX-300 spectrometer at the frequency of 300 MHz. The samples were dissolved in deuterated dimethyl sulfoxide (DMSO- d_6) or deuterated chloroform ($CDCl_3$), depending on the solubility of the materials. The chemical modification degrees (MD) of the esterified products were calculated by the ratio between the areas attributed to the protons bound to the carbon

atoms of the fatty side chain ($A_{CH_2} + A_{CH_3}$) and to the hydrogen atoms of the glycosidic ring of the starch molecule (Eq. 1). When the chemical shift signals of the aliphatic H atoms of the fatty side chain overlap to those of the glycosidic H atoms, a correction factor in the unit of area attributed to the starch protons can be employed [14, 16-18, 20].

$$GMQ = \frac{(A_H)_{fatty\ side-chain}}{(A_H)_{D-glucose}} = \frac{[A_{(n-1)CH_2} + A_{CH_3}]_{(d_{0,8-2,5\ ppm})}}{A_{(d_{3,2-5,1\ ppm})} - y(A_H)_{fatty\ side-chain}} \cdot x$$

where: $(A_H)_{fatty\ side\ chain}$ is the sum of the areas related to the chemical shifts of the methylene H atoms ($-CH_2$) and the H atoms bound to the terminal methyl group of the fatty side chain. For a side chain with n C atoms, it should be considered $(n-1)$ $-CH_2$ groups and one $-CH_3$ terminal group; $(A_H)_{D-glucose}$ is the area related to the signals of the seven protons of the glycosidic unit; x is the number of H atoms present in the spectrum's region covering the chemical shifts of the $-CH_2$ groups and the $-CH_3$ terminal group of the fatty side chain; and y is the number of H atoms bound to the fatty side chain that present overlapped chemical shifts with the glycosidic unit signals.

2.3.3. Thermogravimetric analysis (TG)

Thermogravimetric analysis was carried out to determine the degradation temperature of the samples and assess the influence of the degree of chemical modification on the thermal stability of the modified products. The thermal stability of the starch esters was investigated with the TA Instruments Q500 thermogravimetric analyzer (New Castle, USA). The runs were carried out by heating the samples from room temperature to 973 K at the rate of 10°/min under nitrogen atmosphere.

2.3.4. Solubility and rheological behavior of the starch esters in n -paraffin

The solubility of the synthesized products was initially investigated in solvents with different solubility parameters, to observe the change in the inherent hydrophilicity of the polysaccharide. The main objective was to obtain polymers with affinity for n -paraffin, the solvent that would constitute the continuous phase of the non-aqueous drilling fluid. The solubility of the materials was evaluated, according to the method described by Wesslén and Wesslén (2002), in solvents with different solubility parameters (d): water ($d = 48.0\ MPa^{1/2}$), dimethyl sulfoxide DMSO ($d = 26.4\ MPa^{1/2}$), chloroform $CHCl_3$ ($d = 18.7\ MPa^{1/2}$), toluene ($d = 18.3\ MPa^{1/2}$) and

n-paraffin (reference *n*-dodecane $d = 16.2 \text{ MPa}^{1/2}$) (Barton, 1985). The rheological properties of the fatty starch esters in the presence of *n*-paraffin were assessed by measuring the viscosity in TA Instruments AR 2000 rotational rheometer (New Castle, USA) equipped with parallel plates, at the concentration of 10 % (wt/v) and temperature of 333 K.

3. Results and Discussion

The FTIR spectroscopy permitted the structural characterization of modified starches. The samples were previously purified to extract the unreacted vinyl ester. Fig. 1 shows the characteristic absorption bands of the pre-gelatinized starch structures and the products obtained by using vinyl stearate (a) and vinyl laurate (b) reagents. The synthesized materials spectra presented similar profiles, compatible with the chemical structure found in the literature (Fig. 2) [16, 17]. The incorporation of lauryl and stearyl units in the starch structure was confirmed by the appearance of new absorption bands at $1740\text{--}1745 \text{ cm}^{-1}$, attributed to the carbonyl of the ester [16, 18–20, 22–24]. The peaks present at 2920 cm^{-1} and 2850 cm^{-1} are associated with C–H stretching of the alkyl groups contained in the fatty side chains. The characteristic absorptions of the polysaccharide chain can be observed in the region of $1250\text{--}900 \text{ cm}^{-1}$ (axial deformation of C–O bonds). The bands at $3000\text{--}3600 \text{ cm}^{-1}$ and 1640 cm^{-1} are related to the vibrational stretching of the starch hydroxyl groups, which diminishes in intensity with chemical modification [22].

Fig. 3 shows ^1H NMR spectra of the pre-gelatinized starch and starch fatty esters obtained from vinyl stearate reagent. Seven protons associated with the

D-glucose unit can be seen in the region between 3.2–5.1 ppm [16–17, 20]. The chemical shifts in the range of 0.8–2.5 ppm in the starch fatty esters were associated with aliphatic hydrogen atoms of the fatty side chain [10]. The signals of three protons of the terminal methyl group ($-\text{CH}_3$) of the acyl chain appear as a triplet at 0.865 ppm [16–17]. The chemical shifts displayed by starch laurate samples were essentially the same. The values found for the chemical modification degrees (MD) were 0.65, 2.64, 2.96, 0.62, 2.75 and 2.94 for the products SVS-01, SVS-02, SVS-03, SVL-01, SVL-02 and SVL-03, respectively.

Figs. 4a and 4b show the overlap of the thermogravimetric (TG) curves for the pre-gelatinized starch and the products obtained with vinyl stearate and vinyl laurate, respectively. The chemical modification increased the thermal stability and the total percentage mass loss of the materials, with the lowest quantity of residues at 973 K [17, 25]. While the native starch presented an initial decomposition temperature (T_{onset}) of around 558 K, the derivatives remained stable up to the temperature of 613 K. The starch fatty esters and the vinyl stearate and vinyl laurate reagents presented different thermal degradation characteristics. While the synthesized materials showed a single thermal decomposition stage, there were two mass loss stages for both reagents. There were no significant differences between the thermal behavior of the estearyl and lauryl derivatives, which were obtained at the same vinyl ether/starch molar ratio [26]. The increase in the thermal stability of the derivatives can be attributed to the reduction of the number of hydroxyl groups and the increase in the molar mass and the number of covalent bonds after the esterification reaction [26, 27].

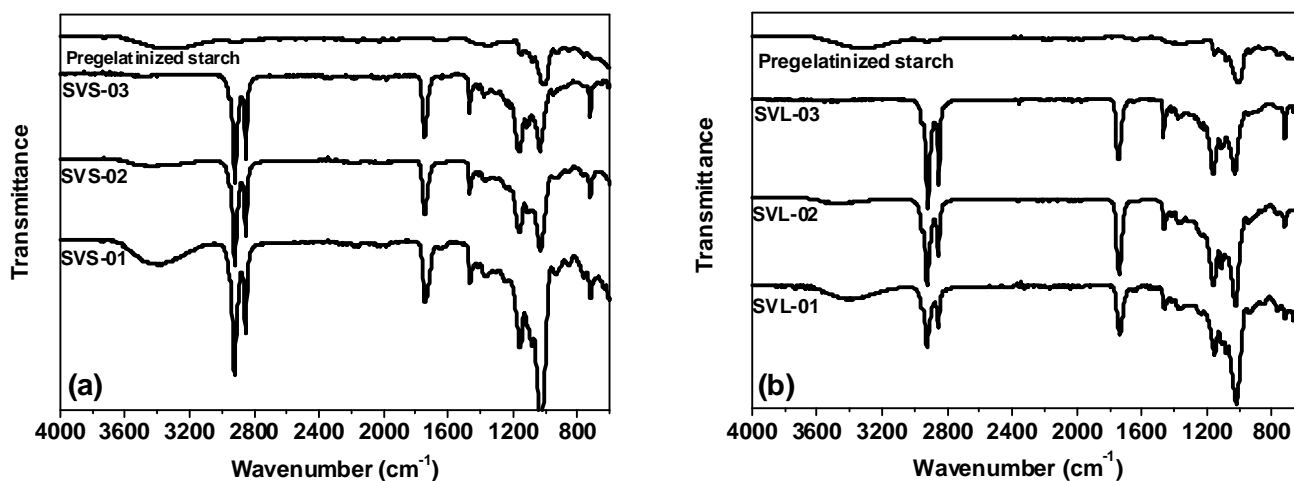


Fig. 1. Infrared absorption spectra of the pre-gelatinized starch and the products obtained from vinyl stearate (SVS-01, SVS-02 and SVS-03) (a) and vinyl laurate (SVL-01, SVL-02 and SVL-03) (b)

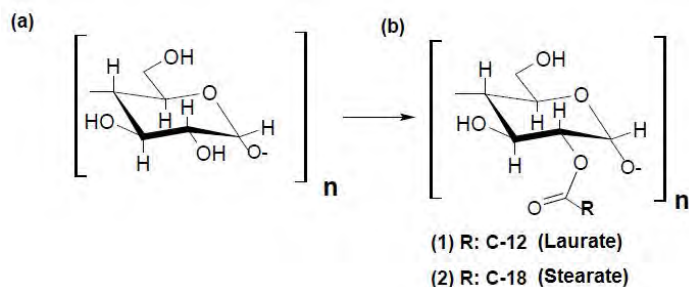


Fig. 2. Schematic representation of the repeating unit of the polysaccharide before (a) and after chemical modification (b)

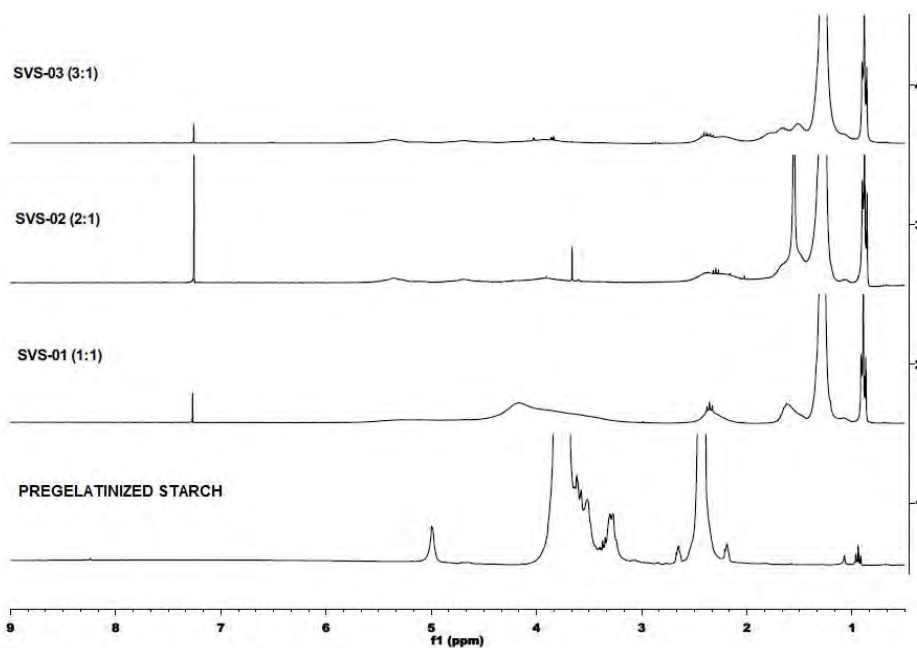


Fig 3. Comparison of the ^1H NMR spectra for the pre-gelatinized starch and the starch fatty esters modified with vinyl stearate (SVS-01, SVS-02 and SVS-03)

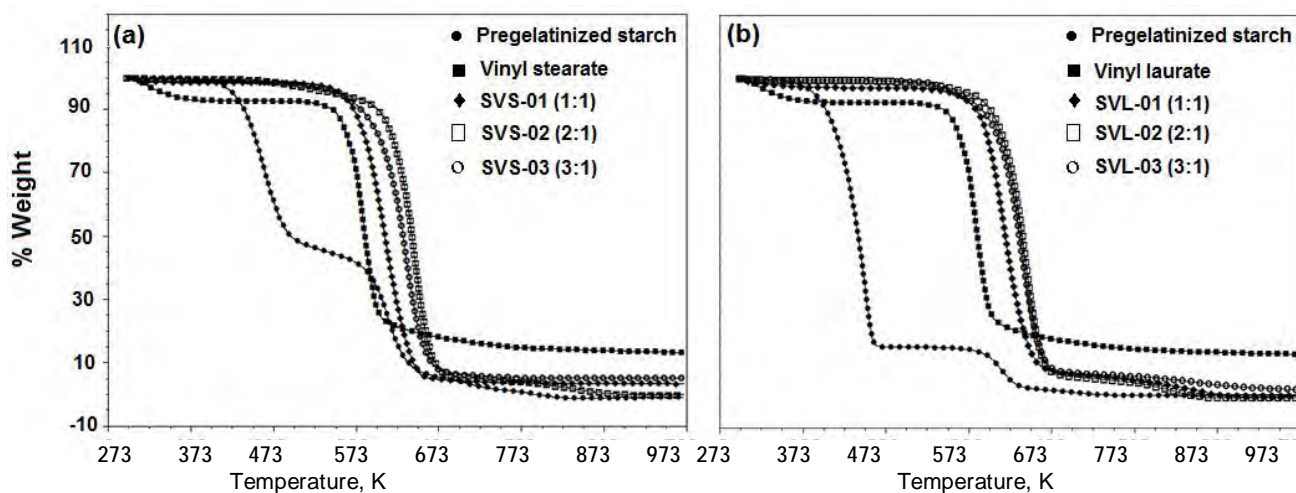


Fig. 4. Overlap of the TG curves for the pre-gelatinized starch and the starch fatty esters modified with vinyl stearate (a) and vinyl laurate (b)

The incorporation of hydrophobic segments in the molecular structure of biopolymers significantly alters the solubility of these compounds [2, 22, 28]. In the present study, the solubility tests showed that the starch derivatives were totally soluble in chloroform and toluene, partially soluble in *n*-paraffin and completely insoluble in water and DMSO. The type of interaction between the starch esters and *n*-paraffin is of basic importance to predict the behavior of these materials as additives for invert emulsion drilling fluids (brine/*n*-paraffin). These additives must have affinity for *n*-paraffin and the tendency to migrate to the interface between the emulsified water droplets and the suspension solids in the fluid [29]. The insertion of hydrocarbon chains in the structure of polysaccharide allowed obtaining polymers with greater affinity for solvents with lower solubility parameters (d), such as chloroform ($d = 18.7$) and toluene ($d = 18.3$). As expected, the increase in MD caused the reduction in the solubility parameter of the modified products. This behavior was confirmed by the partial solubilization of the materials in *n*-paraffin ($d = 16.2$), the solvent with the lowest solubility parameter among those investigated.

The influence of the chemical treatment on the hydrophilicity of the products was also investigated by viscosity measurements in *n*-paraffin. The samples were prepared at concentrations of 1, 5 and 10 % (wt/v) and the tests were carried out at temperatures of 298 and 333 K. All the systems analyzed presented a Newtonian profile and low viscosity values. The material synthesized with vinyl laurate had the higher viscosity than those produced using the vinyl stearate for all the concentrations tested. SVL-01 sample formed heterogeneous dispersions at all concentrations and temperatures tested, which prevented the rheological evaluation of this sample. Since SVS-03 and SVL-03 products became gelled at room temperature, at 5 and 10 % (wt/v) concentrations, the viscosity of their dispersions could only be measured at 333 K.

Fig. 5 shows the viscosity *versus* shear rate profiles for the samples prepared at 10 % (wt/v) and 333 K. Although having a very similar chemical modification degree (MD) to that of SVS-01 (0.65), SVL-01 sample (0.62) was less soluble in *n*-paraffin, probably due to the shorter length of its pendant hydrocarbon chain (C-12). The addition of pregelatinized starch to *n*-paraffin did not cause a significant variation from the viscosity of the pure solvent, attested by the insolubility of the polysaccharide in this medium. As expected, all the systems containing modified material presented the higher viscosity values than pure *n*-paraffin. The molar mass and type of polymer-solvent interaction are fundamental factors for

the variation of a system viscosity. Based on the polymer-solvent interaction and knowledge of the solvent solubility parameter (d), it is possible to infer about d of the polymer material.

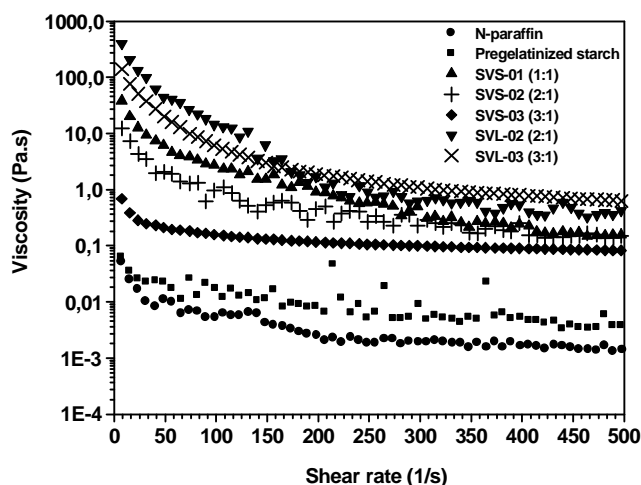


Fig. 5. Viscosity *versus* shear rate profile (333 K) for different samples at 10 % (wt/v)

The degree of chemical modification attained by sample SVL-01 (0.62) probably was not sufficient to promote a substantial reduction of the starch solubility parameter, explaining the low affinity between the polymer and the solvent and the impossibility of rheological characterization of this product. The samples that most raised the viscosity of *n*-paraffin were SVL-02 (MD = 2.75) and SVL-03 (MD = 2.94). This result suggests that these products had the d values nearest to that estimated for *n*-paraffin ($16.2 \text{ MPa}^{1/2}$). Since SVL-02 and SVL-03 have similar MD values, the greater viscosity exhibited by SVL-03 dispersion can be explained by its relatively higher molar mass. The incorporation of a longer pendant group (C-18) more effectively reduced d value, enabling reading the viscosity of the stearyl modified sample with the lowest MD (SVS-01; 0.65). Although having considerably different MD values, samples SVS-01 (0.65) and SVS-02 (2.64) showed very similar viscosity profiles. This behavior can be explained by a competitive effect between the relatively high molar mass of sample SVS-02 (which would be responsible by increasing viscosity) and its respective solubility parameter, which appears to have remained below that attributed to *n*-paraffin (which would be responsible by decreasing viscosity). For sample SVS-03 (2.96), the effects of the molar mass and low d value acted synergistically, weakening the polymer-solvent interaction and contributing to the loss of its rheological property. Good rheology behavior will,

thus, depend on the balance between the contributions of the molar mass and the polymer-solvent interaction: high substitution degrees lead to samples with higher molar masses, and as a result, with greater thickening power; but very high substitution degrees can lead to samples with much lower solubility parameters than the organic solvent, reducing the polymer-solvent interaction and consequently causing lower viscosity values.

4. Conclusions

The incorporation of lauryl and esteryl units in the cornstarch structure was confirmed by the appearance of new absorption bands in the range of 1735–1740 cm^{-1} , attributed to the ester carbonyl function. The chemical modification degrees (MD) of the materials varied from 0.65 to 2.96. The chemical modification contributed to increase the thermal stability and to reduce the inherent hydrophilicity of polysaccharide. From the viscosity measurements of *n*-paraffin, with and without addition of the polymer, it was possible to infer about the polymer-solvent interaction and the variation of the solubility parameter of the modified materials. The highest viscosity values were observed for SVL-02 and SVL-03 samples, probably because they had solubility parameters very close to those estimated for *n*-paraffin. The solubility parameter of the sample SVS-03 appears to be below that attributed to the solvent, which explains the loss of this system rheological property, despite its higher molar mass. The products exhibited potential for application in invert emulsion drilling fluids (brine/*n*-paraffin).

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ЕСТЕРИ ЖИРНИХ КИСЛОТ ТА КРОХМАЛЮ ДЛЯ ПОТЕНЦІЙНОГО ВИКОРИСТАННЯ У НАФТОВІЙ ПРОМИСЛОВОСТІ

Анотація. Отримано і охарактеризовано жирні естери крохмалю при зміні гідрофільно/ліпофільного балансу. Проведено оцінку можливості їх потенційного застосування в бурових розчинах на нафтовій основі. Зміна гідрофобності зразків підтверджена випробуваннями в'язкості, які довели, що продукти мають різні параметри розчинності, поблизу значення розчинника *n*-парафіну.

Ключові слова: модифікований крохмаль, естери жирних кислот, переестерифікація, *n*-парафін, буровий розчин.