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Investigation of the Kinetics of Cotton Soapstock Saponification under Ultrasonic Illumination

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Abstract

This study compares the saponification of cotton soapstock using conventional alkaline and ultrasonic (20 kHz) methods. Experiments were conducted over a temperature range of 333–368 K, with 5 K increments, and agitation times between 15 and 450 min. Under ultrasonic treatment, soapstocks with a free alkalinity of 0.2–0.3% reached the target degree of saponification in approximately 225 min at 358 K and 90 min at 368 K. Under identical conditions, the conventional process required about 270 min and 120 min, respectively. Thus, the application of ultrasound shortened the saponification time by approximately 1.2–1.3 h compared with the classical method. Microscopic analysis showed that ultrasonic irradiation reduced the dispersed phase size from ~2 μm in the conventional process to below the optical resolution limit, indicating a significant improvement in dispersion. Saponification extent was determined for both methods at 15–120 min and 338–368 K. For the conventional method, it increased from 78.78–80.86% to 93.05–98.06%, whereas ultrasound yielded 74.11–74.43% to 92.84–96.88% under the same conditions. Kinetic analysis showed that the apparent activation energy decreased from 21.40 kJ mol^{-1} (conventional) to 18.38 kJ mol^{-1} (ultrasound), demonstrating that ultrasonic treatment lowers the energy barrier and accelerates the reaction. Overall, ultrasound enhances both the rate and efficiency of cotton soapstock saponification, offering a faster and more effective alternative to the classical alkaline process.

1. Introduction

Heterogeneous reactions involving the alkaline hydrolysis of triglycerides, phospholipids, and other saponifiable substances are of considerable theoretical and practical interest for the oil and fat industry. The products of alkaline hydrolysis – fatty acids, soaps, and related compounds – are widely used in cosmetics, pharmaceuticals, detergents, surfactants, and other industrial applications. Since direct alkaline hydrolysis of triglycerides is relatively costly, the use of soapstock, a by-product of oil refining, becomes particularly relevant and economically advantageous for the soap industry.

Soapstock typically contains 20–30% neutral fat, along with sodium salts of fatty acids, minor iron and aluminum carboxylates, phosphatides, higher alcohols, unsaponifiable compounds (waxes, carotenoids, chlorophyll), and silicon-containing impurities. Its complex composition leads to stable emulsions and “native” surfactants, complicating further processing [1–3].

Previous studies have focused on soybean and sunflower soapstocks and their applications in detergents, biofuels, and hydrophobic surfactants [4–5]. The saponification kinetics of sunflower soapstock were investigated at temperatures ranging from 60 to 90 °C over reaction times of 0.5–4 hours. An increase in temperature and reaction time resulted in a rise in soap content from 25.3% to 76.8%, with the process following the Prout–Tompkins kinetic model. Rate

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constants ranged from 3.16×10^{-5} to 9×10^{-5}, and the activation energy was determined to be 39.6 kJ mol^{-1} [6–8]. The thermodynamic parameters of the resulting sodium soaps were determined as follows: $\Delta H = 36.7$ kJ mol^{-1}, $\Delta S = -222$ J mol^{-1} K^{-1}, and $E_a = 39.6$ kJ mol^{-1}.

An efficient method for producing oleate soaps of alkali and alkaline-earth metals (Li, Na, K, Mg, Ca, Ba) via double decomposition under salting-out conditions has been reported [9]. Adding ethanol at ~90 °C increases yields by reducing solubility. Saponification was nearly complete for NaOH (~99%) and LiOH (~98%), but lower for $Ca(OH)_2$ (<95%). IR spectroscopy confirmed product purity and successful ion exchange. The lower calcium soap yield is attributed to limited water availability or non-optimized procedures for calcium systems [9]. One approach to intensifying oil and fat saponification is the use of cavitation and ultrasound. In this context, sonochemistry represents an accessible and effective method for accelerating reactions and enhancing their performance [10, 11].

Sonochemistry involves the study of chemical transformations induced or enhanced by high-intensity ultrasound (20 kHz–10 MHz). The chemical effects do not arise from direct interaction between ultrasound and molecules, but rather from nonlinear acoustic phenomena, particularly acoustic cavitation [10, 11]. The saponification of soybean oil in a 3% KOH solution under ultrasound at 308 ± 2 K for 180 min has been investigated [12]. Experiments conducted at 35 ± 3 kHz and 120 W (Model Dakshin D2) examined the individual and combined influences of stirring, sonication, and displacement on the degree of saponification. It was found that mixing alone yielded 5–53% conversion, sonication alone produced 18–70%, and the combined action of mixing and ultrasound achieved 27–99%.

Ultrasound-assisted alkaline hydrolysis of sunflower oil triglycerides has been studied using underwater irradiation at 35 kHz and 85 W. Under these conditions, high reaction yields were obtained at room temperature within just 15 min of full-power operation, with no detectable by-products. The activation energy required to initiate the reaction under optimal conditions was estimated at 45 kJ, based on ultrasonic probe power measurements [13].

The saponification of castor, almond, and coconut oils has been investigated under ultrasonic irradiation in the presence of phase-transfer catalysts such as acetyltrimethylammonium bromide, benzyltriethylammonium chloride, and tetrabutylammonium bromide [14]. In these experiments, 50 mL of a 3% KOH solution was used, and the degree of saponification was evaluated as a function of time, temperature, and catalyst type. Sonication was applied at 20 and 900 kHz with a constant power of 29.6 W. The saponification yield increased with temperature, reaching up to 94% at 333 K after 12 min at 20 kHz.

A model system consisting of sunflower soapstock and caustic soda was investigated in a previous study on sunflower soapstock saponification [15]. Experiments were carried out at 333 and 353 K, with reaction times of 0–25 min under mechanical stirring (frame stirrer) and ultrasonic irradiation (22 kHz, 30 $W \cdot dm^{-3}$). Kinetic parameters were calculated using the Arrhenius equation. The rate constants during stages I and II were found to be 1.23–1.24 min^{-1} under mechanical stirring and 1.25–1.26 min^{-1} under ultrasonic treatment. Ultrasound shortened the induction period and increased the saponification degree to 98% within 25 min, enhancing the reaction rate by more than 1.8 times. This demonstrates the potential of ultrasonic treatment as an efficient and environmentally friendly intensification method for industrial applications. However, to date, establishing optimal conditions for the saponification of cotton soapstock remains a challenging and highly relevant task. Cotton soapstock represents a complex colloidal system that contains undesirable saponifiable components such as gossypolates and phospholipids. Unlike soapstocks derived from sunflower, soybean, palm, cocoa, or almond oils, the saponification of cotton soapstock requires significantly longer processing times, typically 5–6 h [16].

The difficulty of saponification is further compounded by variations in soapstock composition, which depend on the nature of the refined oil, the level of impurities, and the technological parameters of the neutralization stage. These parameters include the type of alkaline solutions used (NaOH, KOH, sodium aluminate), the application of alkali-like adsorbents (Na_2SiO_3), acid treatments (citric or phosphoric acid), and bleaching agents (bentonite clay, kaolin, activated carbon) [17–19]. A study reported in [20] examined the fractional separation of saponified cotton soapstock into gossypolates and soap.

Reference [21] describes improvements and optimization of the soapstock-splitting process using 45% NaOH in a 20 m^3 soapstock reactor, operating at 393–422 K and equipped with heat exchangers, a saponification column, an intermediate tank, and a soapstock separation reactor. Under these conditions, the resulting fatty acids exhibited a potassium hydroxide (KOH) value of 171 mg/g, demonstrating a high degree of saponification and product purity.

At JSC "Urganch yog'-moy" (Uzbekistan), saponification is performed in a 30 m^3 soapstock vessel at 303–313 K and 3 atm using 42% NaOH, heat exchangers, and an 8 kW circulation pump. The process requires 4–6 h and consumes approximately 125.5 kg of steam per ton of soapstock [22].

The processing of cottonseed soapstock is of considerable industrial importance, especially for the production of crude fatty acids. Uzbekistan annually produces more than 2.5 million tons of raw cotton, of which approximately 50% (1.25 million tons) is processed into cottonseed for oil extraction. On average, one ton of cottonseed yields about 190 kg of crude oil (19%). From 1.25 million tons of seeds produced in the country, accounting for processing losses, approximately 0.22 million tons of refined oil and 0.022 million tons of soapstock are obtained

Following on from the preceding, the goal of this work is to calculate the thermodynamic constants of cotton soapstock, which is barely saponifiable, using ultrasonic treatment.

As noted earlier, this study proposes a novel and simplified saponification strategy based on ultrasonic irradiation, which significantly reduces reaction time without the need for additional catalysts or complex equipment. The approach offers a sustainable and energy-efficient alternative by lowering heat and electricity consumption while simultaneously improving the yield of crude fatty acids such as oleic, palmitic, and linoleic acids.

The findings further demonstrate that ultrasonic treatment enhances the overall efficiency of the saponification process, enabling shorter reaction times and eliminating the requirement for auxiliary catalysts or specialized equipment. This makes the method both environmentally and economically advantageous.

2. Study Objects and Methods

The object of this study was cotton soapstock obtained from JSC "Urganch yog'-moy". For laboratory experiments, the soapstock was diluted 1:1 with water of 7 mmol equiv/L hardness. After dilution, it contained 35.1% total fat, 9.9% neutral fat, and 55% water [22, 23]. Moisture content, volatile substances, neutral fat, crude fatty acids, and unsaponifiable substances were determined according to [24]. Preparation of samples for chromatographic analysis of fatty acid composition followed the procedure in [25]. Fatty acids (FA) were analyzed in the form of methyl esters by gas chromatography using an Agilent 6890 N instrument equipped with a flame ionization detector and a 30 m × 0.32 mm capillary column with HP-5 stationary phase. Helium was used as the carrier gas, and the temperature program ranged from 150 to 270 °C.

The pH of the diluted soapstock was measured with a Mettler Toledo FiveGo pH meter (Switzerland). The initial soapstock had a pH of 9.68 (average of three measurements), which increased to 10.87 after saponification. IR spectra of the feedstock and saponified soapstock were recorded on a JASCO FTIR-6x spectrometer (Japan) in the range 400–4000 cm^{-1} with a resolution of 0.25 cm^{-1}. This spectrometer allows analysis of both solid and liquid samples without using compressed KBr tablets. Peak matching was performed using Thermo Galactic GRAMS/AI software (2003). For comparison, saponification was carried out using both the classical method and an ultrasonic installation (Cavitator Ultrasonic Cleaner USC-3L, China) operating at 220 VAC/20 kHz, 100 W.

The saponification process is illustrated in Fig. 1. Raw soapstock (1500 g; density 1.3402 g/cm^3, viscosity 1.94 cP) was loaded into a 2000-ml stainless steel reactor (grade X18N10T) equipped with an ultrasonic device, grounding, and a circulation pump (0.5 kWh, 0.2 m^3/min). The pump circulated the soapstock through a 10 mm stainless steel pipe (grade X18N10T) passing through a heat exchanger maintained at 373 K and exposed to ultrasonic waves at 20 kHz.

A 40% NaOH solution was gradually supplied via Mariotte flasks (9). Temperature was controlled by a thermostat (15) connected to relays (3, 17) and operated through an electrical panel (4), with relays mounted on a tripod (18). Circulation of the saponified mass was maintained by pump (11) through the pipe (12), tripod (16), and heat exchanger (13), powered via a transformer shield (14).

Simultaneously, steam at 421 K and 3 atm (7) was introduced from the reactor bottom through tube (6) to enhance mixing. A condensate vessel ensured a continuous supply of live steam at 421 K. Auxiliary components (6–9) were fixed using tripod supports (10). The state and particle size of dispersed phases in both raw and saponified samples were examined microscopically using a BioBlue S/N-EC 2209881 instrument (Euromex, Netherlands) with SP 40/0.65 and 160/0.17 lenses. Unlike previous setups [26], this microscope is equipped with a device for particle size measurement.

The saponification process was studied over a temperature range of 333–368 K with 5 K increments, and contact times of 15–450 min at a constant atmospheric pressure of 0.1 MPa.

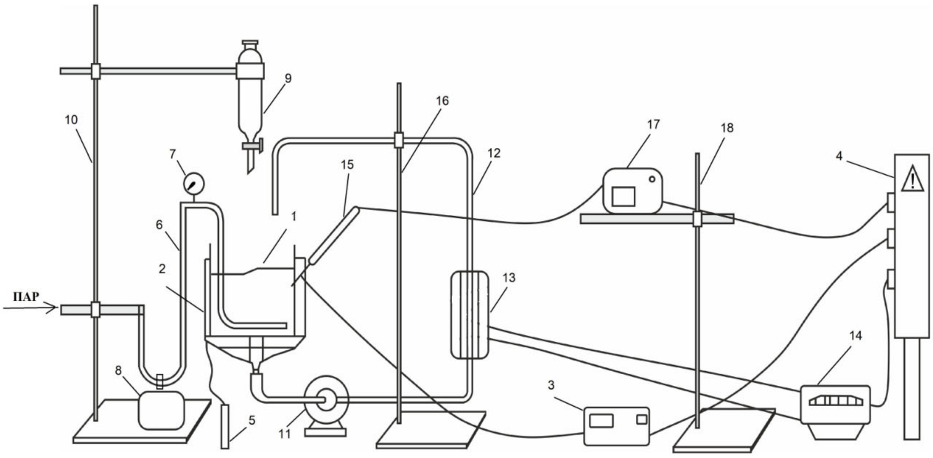


Fig. 1. Laboratory model plant for saponification of cotton soapstock using ultrasonic treatment: 1 – vessel for soap stock saponification; 2 – ultrasound shirt; 3 – relay; 4 – electrical panel; 5 – grounding; 6 – steam tube; 7 – pressure gauge; 8 – vessel for condensate; 9 – dispenser for NaOH; 10 – tripod; 11 – pump; 12 – circulation pipe; 13 – heat exchanger; 14 – transformer shield; 15 – thermostat; 16 – tripod; 17 – relay; 18 – tripod.

A 400 mL conical flask was used to weigh 5–10 g of the soap-alkaline solution with an accuracy of 0.01 g, depending on its free alkali content. To the flask, 50 mL of 96% pre-neutralized alcohol and 2–3 drops of 1% phenolphthalein alcohol solution were added. The mixture was titrated with 0.1 N HCl under vigorous shaking until the pink color disappeared. The sample size was chosen to ensure that the alcohol concentration remained ≥60% after titration [27].

The free alkalinity (FA, %) was calculated using Eq. (1) [27]:

$$x = \frac{0.004 \cdot V \cdot K}{P} \cdot 100 \qquad (1)$$

where 0.004 is the mass of alkali corresponding to 1 mL of 0.1 N HCl (g), V is the volume of HCl used (mL), K is the titrant correction factor, and P is the mass of the soap-alkaline sample (g).

The saponification extent (SE) of the reaction mixture, in contrast to the approaches reported in Refs. [12, 14, 28], was determined using a standard stoichiometric relationship commonly applied in analytical chemistry. In this approach, the concentration (C_1) and volume (V_1) of the titrated substance are directly proportional to the concentration (C_2) and volume (V_2) of the titrant, as expressed in Eq. (2):

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad (2)$$

Given the concentration and volume of hydrochloric acid from Eq. (3)

$$C_1 \cdot V_1 = C_2 \cdot V_2 \qquad (3)$$

from which through the Eq. (4):

$$C_2 = \frac{n_{ecv}}{V_2} \qquad (4)$$

The mass of free alkali was calculated using Eq. (5):

$$m = n \cdot M_r \qquad (5)$$

where m is the mass of the substance (g); n is the amount of substance (mol); M_r is the relative molar mass (g/mol).

The mass of alkali required for the saponification of triglycerides and free fatty acids was then calculated using Eqs. (6) and (7). The resulting soaps were subsequently subjected to sulfuric acid decomposition according to Eq. (8) [15]:

$$C_3H_5(RCOO)_{3(s)} + 3NaOH_{(aq)} \rightarrow 3RCOONa_{(aq)} + C_3H_5(OH)_{3(aq)} \qquad (6)$$

$$RCOOH_{(s)} + NaOH_{(aq)} \rightarrow RCOONa_{(aq)} + H_2O_{(l)} \qquad (7)$$

$$2RCOONa_{(aq)} + H_2SO_{4(aq)} \rightarrow 2RCOOH_{(s)} + Na_2SO_{4(aq)} \qquad (8)$$

Thus, the formula for determining the saponification efficiency (SE, %) is derived by Eq. (9)

$$SE = \frac{m_1 - m_2}{m_1} \% \qquad (9)$$

where m_1 is the total mass of alkali (g) required stoichiometrically for the saponification of triglycerides and fatty acids in the soapstock, and; m_2 is the mass of free alkali (g) determined by titration of the soapstock sample with 0.1 N HCl.

All experiments were carried out in triplicate, and the mean values are reported.

3. Results and Discussion

The dependence of free alkalinity (FA) of cotton soapstock on temperature and reaction time, using both the classical and ultrasonic methods, is shown in Figs. 2 and 3 with error bars.

According to Fig. 2, the classical saponification technique shows slower progress at low temperatures and during prolonged contact times between triglycerides and free fatty acids. As reported in [27], the FA content in soapstock should ideally reach 0.2–0.3%. The linear dependence of FA in the classical method indicates that increasing the temperature accelerates saponification, with FA increasing from 0.609% at 333 K to 2.36% at 368 K after 15 min, an almost 3.87-fold increase. A notable increase of FA to 0.265% occurs at 353 K after 390 min, approaching the target range of 0.2–0.3%. This effect is attributed to the increase in the rate constant of the saponification reaction with temperature. According to the equations shown in Fig. 2, the correlation coefficient R^2 ranges from 0.9021 to 0.9966.

A similar trend is observed for ultrasonic-assisted saponification (Fig. 3). For a temperature increase from 60 to 95 °C under ultrasonic conditions (220 VAC, 20 kHz, 15 min), FA rises by up to 3.43 times, decreasing from 2.03% to 0.591%. This demonstrates that ultrasonic treatment accelerates the saponification process, achieving the desired FA concentration more efficiently.

An increase in saponification time at constant temperatures leads to a progressive increase in FA. The changes in FA over contact times of 15–450 min at temperatures of 333, 338, 343, 348, 353, 358, 363, and 368 K are as follows:

- At 333 K, FA increased from 2.03% to 1.21% over 15–450 min.
- At 338 K, FA increased from 1.804% to 1.36% over 15–450 min.
- At 343 K, FA increased from 1.561% to 4.22% over 15–375 min.
- At 348 K, FA increased from 1.441% to 5.07% over 15–360 min.
- At 353 K, FA increased from 1.35% to 5.47% over 15–330 min.
- At 358 K, FA increased from 1.097% to 5.10% over 15–240 min.
- At 363 K, FA increased from 0.911% to 3.31% over 15–165 min.
- At 368 K, FA increased from 0.591% to 3.79% over 15–120 min.

Considering that the required FA content should be maintained within 0.2–0.3%, Figs. 2 and 3 show that under the conventional method, this level is reached at different times depending on temperature: 120, 180, 270, and 390 min at 368, 363, 358, and 353 K, respectively. Using ultrasound (220 VAC, 20 kHz), the required FA is achieved faster: 90, 150, 225, 330, and 360 min at 368, 363, 358, 353, and 348 K, respectively.

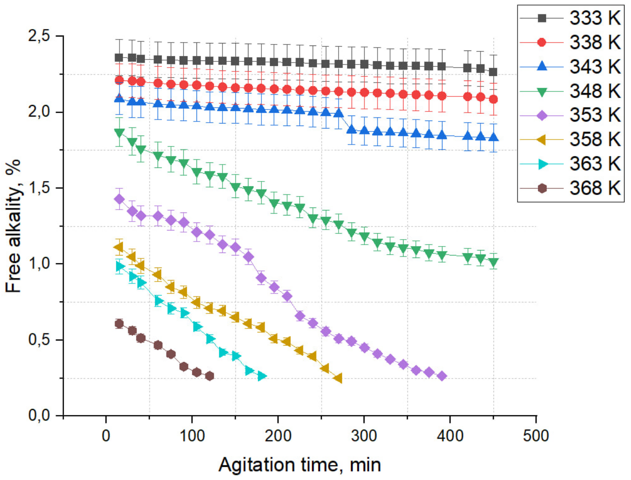


Fig. 2. Change in the free alkalinity of the soapstock, saponified by the conventional method, depending on the agitation time and temperature.

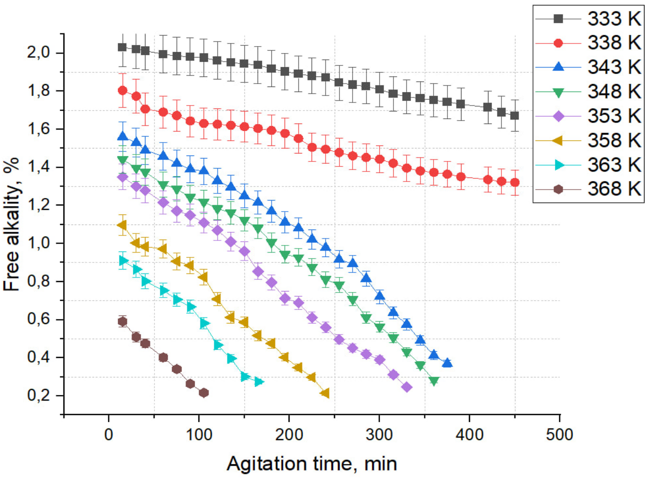


Fig. 3. Change in the free alkalinity of the soapstock, saponified by the ultrasonic method depending on the agitation time and temperature.

Using the conventional method, the required FA of 0.265% is reached in 390 min at 353 K, while at 368 K the same FA level is achieved in only 120 min. At 358 K, the target FA of 0.251% is typically attained after 270 min.

Under ultrasonic treatment, the desired FA of 0.284% is reached after 360 min at a minimum temperature of 75 °C. At higher temperatures, FA of 0.264% is achieved in under 90 min at 368 K, while at 358 K it takes approximately 225 min.

The data show that free alkalinity (FA) reaches the target value at 363–368 K using the conventional method. As reported in [16], this typically requires 6–8 h of saponification. Under laboratory conditions, the time required to reach the target FA was approximately 4.5 h.

Using the ultrasonic method, the saponification time to achieve the required FA was 3.75 h, representing a time saving of about 1.2 h. This reduction is attributed to a decrease in the size of fatty acid molecules under acoustic forces, which improves particle dispersion in the soapstock [14]. Dispersed fatty acid molecules collide more easily with alkali ions, preventing the formation of obstructive soap films that can slow saponification.

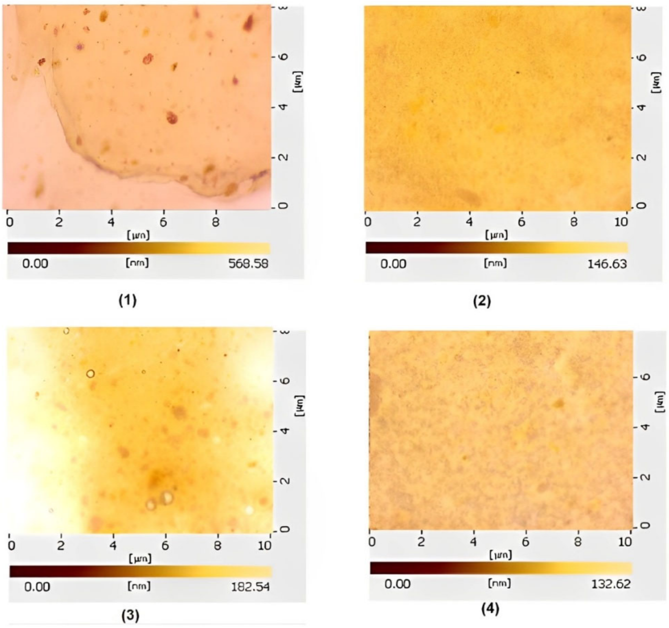
Morphological investigations of the soapstock's dispersed phases are shown in Fig. 4. The soapstock contains approximately 60% water, forming a dispersed medium in which Na-soap is partially dissolved. Figure 4 illustrates the particles of the dispersed phase in the raw soapstock. A clear boundary exists between the aqueous phase and the fatty phase, which includes neutral fats. Within the fatty phase, dispersed particles are present that are insoluble in both water and soapstock fat. These consist of unsaponifiable substances (waxes, pigments, sterols, styrenes, etc.) and mechanical impurities, with particle sizes ranging from 0.3 to 2 μm.

Ultrasonic treatment (220 VAC, 20 kHz) leads to complete dispersion of solid particles, resulting in a homogeneous phase. Thus, ultrasound acts as an emulsifying agent. Microphotographs of soapstock saponified by the conventional method show spherical dispersed phases of neutral fat (oil) in the aqueous medium. The dispersed phase particles range in size from 0.1 to 1.0 μm.

The appearance of a droplet of oils in the soap stock indicates an insufficient saponification process, although the FA was 0.2–0.3%. However, in the case of saponification of the soapstock under ultrasonic action, traces of dispersed phases with a particle size of less than 0.01 μm are observed. This phenomenon may be explained by the fact that the scattered phases are destroyed and their smaller particles are created by the acoustic vibrations of ultrasound. A suitable environment for the saponification of fatty acid molecules and oil is therefore created in the soapstock. To prove how much the interaction between sodium alkali and fatty acid molecules occurs.

Previously, the saponification extent was calculated within a shorter contact time range of 15 to 120 min and at temperatures between 333 and 368 K, as shown in Tables S1 and S2 with statistical parameters, including standard deviations, standard errors, and 95% confidence intervals. Calculating the rate constant of the saponification process was made feasible by experimental numerical data on the saponification extent shown in Figs. 5 and 6. In addition 3D descriptions are presented in Figs. S1 and S2.

Using the conventional method (Table S1), increasing the saponification time from 15 to 120 min reduced FA as follows: from 2.21 to 2.17% at 338 K, from 1.87 to 1.59% at 348 K, from 1.11 to 0.71% at 358 K, and from 0.61 to 0.27% at 368 K.



(1) (2) (3) (4)

Fig. 4. Electron microscopic images of raw soapstock (1) and (2), saponified soapstock by conventional (3) and ultrasonic (4) methods (magnification 40 times).

Under ultrasonic treatment (Table S2), a similar trend was observed: increasing the saponification time from 15 to 120 min led to a decrease in FA content from 1.80 to 1.63% at 338 K, from 1.44 to 1.18% at 348 K, from 1.10 to 0.71% at 358 K, and from 0.59 to 0.16% at 368 K. For the conventional saponification process, temperature exerted a stronger influence on the saponification extent than reaction time. At 333 K, extending the reaction time from 15 to 120 min resulted in only a slight increase in the saponification extent, from 72.23 to 72.49%. In contrast, increasing the temperature from 333 to 368 K for a fixed duration of 15 min raised the saponification extent to 92.84%. Further extending the reaction time to 120 min at temperatures between 353 and 368 K resulted in maximum saponification extents of 85.95–96.88%.

Under ultrasonic treatment, acoustic effects significantly enhanced the saponification process. At 333 K, increasing the reaction time from 15 to 120 min raised the saponification extent from 76.12 to 76.93%. At higher temperatures (353–368 K) and longer reaction times (15–120 min), the saponification extent increased substantially, reaching 83.82–93.05% and 86.86–98.06%, respectively, confirming the intensifying effect of ultrasound on the reaction.

The data obtained using the conventional method demonstrated high reproducibility, as evidenced by low standard deviations (0.01–0.14) and standard errors (0.01–0.60) for K, lg K, and $\lg[C/(C_0–C_\tau)]$. The corresponding 95% confidence intervals further confirmed the reliability of the measurements. An increase in temperature led to higher saponification extents and rate constants, with lg K values becoming less negative, indicating accelerated reaction kinetics (Table S1, Fig. 5).

Similarly, the ultrasonic saponification data demonstrated high reproducibility, as indicated by low standard deviations (0.00–0.18) and standard errors (0.00–0.07) for K, lg K, and $\lg[C/(C_0–C_\tau)$. The corresponding 95% confidence intervals further confirmed the reliability of the measurements. An increase in temperature enhanced both the saponification extent and the reaction rate, with less negative lg K values and higher K compared with the conventional method (Table S2).

Overall, both methods yielded statistically reliable kinetic data; however, ultrasonic treatment consistently enhanced reaction rates and saponification efficiency. In general, the heterogeneous saponification reaction (Eqs. 6 and 7) is irreversible and follows second-order kinetics [15, 28], although it can also be described as first-order with respect to each reactant, as expressed by Eq. (10) [29].

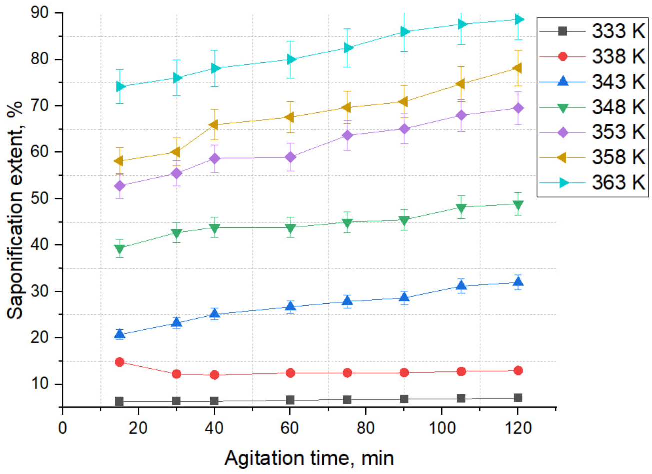


Fig. 5. Change in the saponification extent depending on the agitation time and temperature under the conditions of the conventional method.

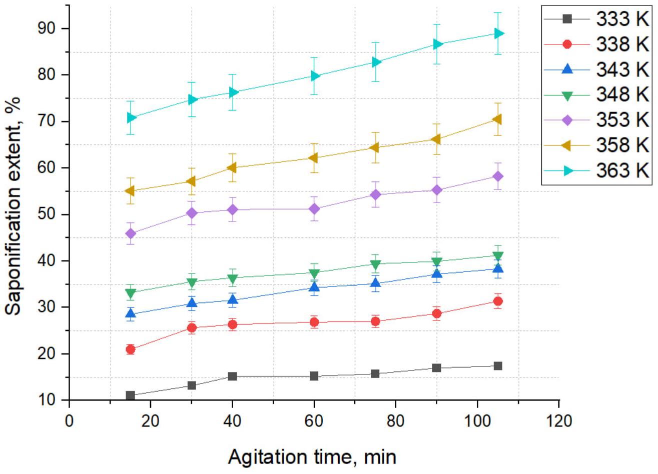


Fig. 6. Change in the degree of saponification depending on the agitation time and temperature under the conditions of the ultrasonic method.

$$\begin{gathered} -r_{NaOH} = -r_{triglyceride} = kC_{NaOH}C_{triglyceride} \\ -r_{NaOH} = -r_{FA} = kC_{NaOH}C_{FA} \end{gathered} \tag{10}$$

Therefore, calculations were performed using the first-order kinetic equation to determine the reaction order of the saponification process according to Eq. (11) [30]:

$$K = \frac{2.303}{\tau} \cdot \lg \frac{C_0}{C_\tau} \tag{11}$$

where C_0 and C_τ represent the expected maximum saponification extent of the soapstock at the initial stage of saponification and after an elapsed time interval (τ), respectively, and K is the saponification rate constant.

The linear dependence of lg[$C/(C_0\text{-}C_\tau)$] on τ indicates that the saponification process, under both conventional and ultrasonic methods, follows first-order kinetics (Tables 1 and 2).

Figures 7 and 8 show the dependence of the average lg K values on the reciprocal temperature, 1/T. As seen in Figs. 7 and 8, the linear relationships, with correlation coefficients of approximately 0.97 and 0.93, confirm the temperature dependence of the reaction rate constant lg K.

Since in the process of saponification, the influence of temperature was observed more than time, the calculation of the saponification rate constant was made, which increased with increasing temperature (Tables S1 and S2) and this dependence obeys the Arrhenius law [31] according to Eq. 12:

$$K = K_0 e^{-E/RT} \tag{12}$$

After applying logarithmic transformation, the following expression is obtained by Eq. (13):

$$lgK = lgK_0 - E/2.303 \cdot 1.987 \cdot 1/T \tag{13}$$

To simplify the expression, the following notation is introduced by Eq. (14):

$$lgK = \eta; lgK_0 = a; = E/2.303 \cdot 1.987 = E/4.184; 1/T = \xi; \eta = \text{ą} - b \cdot \xi \tag{14}$$

Using equation, it makes the following dependencies of the Eqs. (15) and (16):

$$b_{2.1} = \eta_2 - \eta_1/\xi_1 - \xi_2;\ \ b_{3.2} = \eta_3 - \eta_2/\xi_2 - \xi_3 \tag{15}$$

$$b_{3.4} = \eta_3 - \eta_1/\xi_1 - \xi_3\,;\ \ b_{4.1} = \eta_4 - \eta_1/\xi_1 - \xi_4 \tag{16}$$

where

$b_{2.1}$ – means calculations between 75 and 65 °C in Kelvin (348 and 338 K);

$b_{3.2}$ – means calculations between 85 and 75 °C in Kelvin (358 and 348 K);

$b_{3.4}$ – means calculations between 85 and 95 °C in Kelvin (358 and 368 K);

$b_{4.1}$ – means calculations between 95 and 65 °C in Kelvin (368 and 338 K).

Based on the experimental data, the individual values of the parameter 'b' are calculated, and the average value, denoted as "$b_{average}$", is determined Eq. 17:

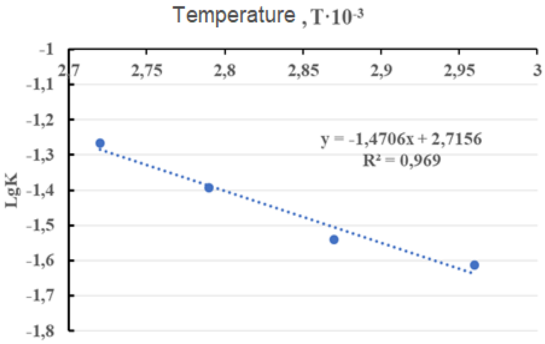


Fig. 7. Dependence of the average value of Lg K on the reciprocal temperature (1/T·10^{-3}) during soapstock saponification by the conventional method.

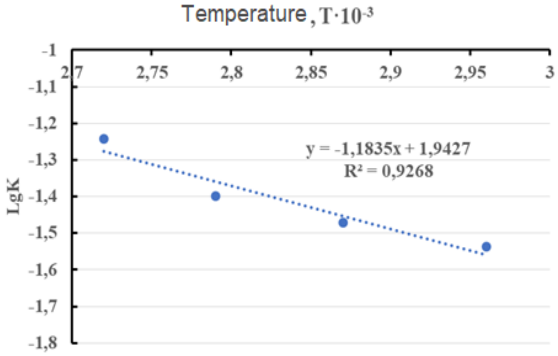


Fig. 8. Dependence of the average value of Lg K on the reciprocal temperature (1/T·10^{-3}) during soapstock saponification by the ultrasonic method.

$$\mathrm{a} = \sum \eta + b \cdot \sum \xi/4 \tag{17}$$

The values of "a" and "b" are inserted into the equation, resulting in the following:

When saponification is carried out by the conventional method using Eqs. (18) and (19):

$$\eta = -5.45243 - 127.506 \cdot \xi \tag{18}$$

$$lgK = -5.45243 - 127.506 \cdot 1/T \tag{19}$$

When saponification is carried out by the ultrasonic method using Eqs. (20) and (21):

$$\eta = -5{,}34076 - 108{,}805 \cdot \xi \tag{20}$$

$$lgK = -5{,}34076 - 108{,}805 \cdot 1/T \tag{21}$$

Table 1. Dependence of the change in the activation energy of the process of saponification of cotton soapstock by convention and ultrasonic methods

T, K	$1/T \cdot 10^{-3}$	Temperature vs. activation energy		Average activation energy	
		E_a, kcal/mol	E_a, kJ/mol	$E_{caverage}$, kcal/mol	$E_{average}$, kJ/mol
1	2	3	4	5	6
When saponified by the convention method					
338	2.959	6.14	25.66	5.12	21.40
348	2.874				
358	2.793	4.10	17.14		
368	2.717				
When saponified by ultrasonic method					
338	2.959	3.86	16.13	4.41	18.38
348	2.874				
358	2.793	4.94	20.64		
368	2.717				

Table 2. Comparison between raw soapstock and saponified soapstock by ultrasound method

#	Frequencies (cm^{-1})		
	Crude soapstock	By ultrasound method	Assignments
1	3401.82	3410.27	Broad absorption of stretching vibration O–H
2	3009.37	3022.87	Stretching = CH–H
3	2947.66	2947.66	Asymmetric stretching CH_3, C–H
4	2920.66	2921.63	Asymmetric stretching CH_2, C–H
5	2852.2	2852.2	Symmetric stretching CH_2, C–H
6	1554.34	1554.34	Asymmetric stretching COO^-, C–O (ω_2)
7	1487.81	1484.92	Deformation CH_2
8	1413.57	1410.67	Symmetric stretching COO^-, C–O (ω_1)
9	1313.29	1330.64	Deformation CH_2, adjacent to COO^-
10	1130.08	1106.94	Glycerin
11	725.104	721.247	Vibration $(CH_2)n$, n > 4
12	422.334	486.938	Metal bond–O

A first-order kinetic model was applied for soapstock saponification, consistent with the linear dependence of ln ($C_0/(C_0\text{-}C_\tau)$) on time (τ) for both conventional and ultrasonic methods (Tables 1 and 2). The temperature dependence of the reaction rate constants (lg K) is shown in Figs. 7 and 8, with high correlation coefficients ($R^2 \approx 0.97$ for conventional, $R^2 \approx 0.93$ for ultrasonic) and residuals randomly distributed, confirming the adequacy of the first-order assumption. Arrhenius analysis yielded meaningful activation energies, and overall, the experimental data are well-described by the first-order model despite the heterogeneous nature of the system.

Using two Arrhenius plots above, we can extract the following data and build an example of how our model fitting and residuals section can look.

Conventional saponification → slope = –1.4706, intercept = 2.7156, $R^2 = 0.969$

Ultrasonic saponification → slope = –1.1835, intercept = 1.9427, $R^2 = 0.9268$

Comparison of experimental and calculated rate constants and residuals for conventional and ultrasonic saponification processes are given in Table S3.

In our case, depending on the temperature and time of saponification of cotton soapstock by convention and ultrasonic methods demonstrate that the average apparent activation energy values are 5.12 kcal/mol or 21.40 kJ/mol and 4.41 kcal/mol or 18.38 kJ, respectively. This means that ultrasonic treatment requires approximately 1.2 times less energy when saponifying cotton soapstock.

The apparent activation energies obtained from the Arrhenius plots were 21.40 kJ·mol^{-1} for the conventional process and 18.38 kJ·mol^{-1} under ultrasonic treatment. Although the numerical difference (3.02 kJ·mol^{-1}) appears small, it exceeds the estimated experimental uncertainty (±1 kJ·mol^{-1}) and results in a roughly 3.4-fold higher rate constant at 298 K, according to the Arrhenius equation. Therefore, the reduction in activation energy can be regarded as statistically significant and industrially meaningful, indicating that ultrasonic activation effectively lowers the energy barrier and accelerates the saponification reaction.

The IR spectra of raw soapstock and soapstock saponified using ultrasonic treatment are shown in Fig. 9(a) and (b), respectively, while the corresponding vibrational frequencies are summarized in Table 2. The FTIR spectra clearly demonstrate the molecular transformations occurring during the saponification process. In the raw soapstock sample, the broad absorption band near 3400 cm^{-1} is attributed to O–H stretching vibrations of bound water and hydrogen-bonded hydroxyl groups. The intense band at 1745 cm^{-1} corresponds to C=O stretching vibrations of ester groups in triglycerides, confirming the presence of unreacted fats. The aliphatic C–H stretching bands observed at 2920 and 2850 cm^{-1}, assigned to asymmetric (v_as, ω_2) and symmetric (v_s, ω_1) stretching vibrations of CH_2 and CH_3 groups, respectively, remain largely unchanged, indicating preservation of the hydrocarbon backbone.

After ultrasonic activation, pronounced spectral changes confirm the progress of saponification. The ester carbonyl band at ~1740 cm^{-1} decreases sharply, indicating cleavage of ester bonds and formation of fatty acid salts. Concurrently, the COO^- bands at 1554 cm^{-1} (asymmetric) and 1485–1411 cm^{-1} (symmetric) intensify, reflecting the generation of carboxylate anions coordinated with Na^+, a characteristic feature of soap formation. The C–O stretching band shifts from 1130 to 1107 cm^{-1}, consistent with the release of free glycerol, while the CH_2 bending vibration moves from 1313 to ~1330 cm^{-1}, indicating structural rearrangement of the acyl chains. The new low-frequency band at ~487 cm^{-1} assigned to Na–O stretching, further confirms the formation of sodium carboxylate linkages in the product.

These transformations–loss of ester C=O, emergence of COO^- doublets, and glycerol band shifts–trace the full progression from triglycerides to soap

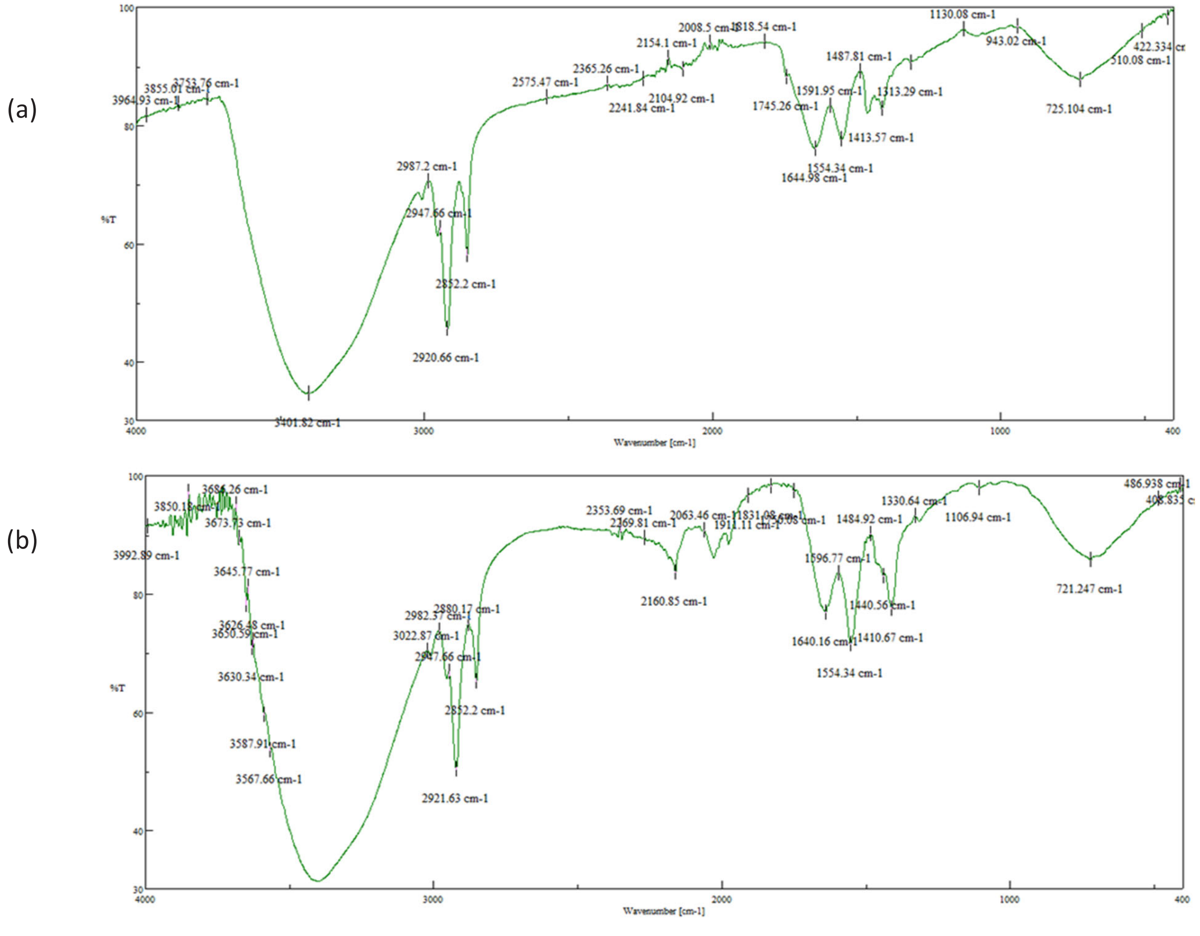


Fig. 9. IR spectra of raw soapstock (a) and ultrasound saponified soapstock (b).

Table 3. Comparison of Energy Indicators (5 h vs. 3.75 h)

Working time, h	Pump electricity, kWh	Ultrasonic energy, kWh	Specific energy, kWh/t	Heat energy, kWh/t	Electricity cost
5	40.0	–	1.492	1984.39	30.375 UZS (~ 2,97 USD)
3.75	30.0	0.375	1.119	1984.39	27.338 UZS (~ 2,26 USD)

and glycerol. The strengthened COO^- and Na–O absorptions validate the formation of ionic soap structures. Correlation with kinetic data (rising SE%) confirms that ultrasound accelerates ester cleavage and salt formation, enhancing molecular contact and reaction completeness. Overall, the FTIR spectra provide direct molecular evidence of the saponification pathway and demonstrate the synergistic mechanochemical effect of ultrasound in promoting rapid and efficient soap formation.

Below is a complete calculation of the energy consumption and technical-economic indicators for saponification of soapstock (20 m^3).

1. Initial data

- Tank volume: 30 m^3 (working volume 20 m^3)
- Soapstock density: 1.3402 g/cm^3 (1340.2 kg/m^3)
- Batch weight: 20 m^3 × 1340.2 kg/m^3 = 26.804 t
- Viscosity: 1.94 cP at 60 °C
- Pump: Sh 40-4-19.5/4, power 8 kW, head 18 m, working pressure 6 kgf/cm^2
- Steam parameters: pressure 3 atm, temperature 144 °C, flow rate 125 kg/t soapstock
- Circulation time: 5 h (conventional method) and 3.75 h (ultrasonic method).
- Ultrasound device: power 100 W (0.1 kW), frequency 20 kHz

2. Steam and Heat Consumption

- Total steam consumption per batch: 26.804 t × 125 kg/t = 3.350.5 kg
- Latent heat of condensation: h_{fg} = 2.132.16 kJ/kg
- Total steam energy: 3.350.5 kg × 2.132.16 kJ/kg = 7.143.802 kJ ≈ 1.984.39 kWh

3. Pump Electricity Consumption

- Conventional method (5 h): 8 kW × 5 h = 40 kWh (≈ 1.492 kWh/t)
- Ultrasonic method (3.75 h): 8 kW × 3.75 h = 30 kWh (≈ 1.119 kWh/t)

4. Comparison of Energy Indicators (Table 3)

- Electricity savings: 10 kWh (≈ 25%)
- Heat savings: 0 kWh (steam rate fixed)
- Although the total thermal energy demand remains unchanged, the reduced processing time implies a higher instantaneous heat input rate (approximately +33.3%), which must be considered in boiler operation and heat transfer design.

5. Economic calculation (Uzbekistan, 2025)

- Electricity tariff: 900 UZS/kWh
  Pump electricity cost
- 5 h: 36.000 UZS
- 3.75 h: 27.000 UZS
- Savings: 9.000 UZS
  Steam/heat cost (boiler efficiency 85%)
- Total heat cost: 2.102.184 UZS
- Savings: 0 UZS

Reducing circulation time via ultrasonic treatment provides electricity savings of approximately 10 kWh (≈25%), while heat consumption remains constant due to the fixed steam rate per ton of product. To achieve additional heat savings, strategies such as condensate recovery or reducing steam consumption are recommended.

3. Conclusion

Thus, the saponification of cotton soapstock, which proceeds in a heterogeneous reaction medium, requires additional approaches to accelerate the process. Due to the complex multicomponent nature of cotton soapstock, conventional saponification methods require longer reaction times and higher temperatures to achieve the desired free alkalinity (FA). In contrast, ultrasonic treatment has a beneficial effect on this multicomponent system.

Comparative microscopic analysis shows that ultrasonic treatment promotes pronounced particle dispersion, reducing particle sizes to below 0.01 μm. By comparison, saponification carried out using the classical method results in dispersed phase particle sizes in the range of 0.3–2 μm. This behavior can be attributed to the enhancement of intermolecular interactions under ultrasonic irradiation, which destabilizes aggregated structures within the complex colloidal system of cotton soapstock.

Furthermore, ultrasonic action partially acts as an emulsification mechanism, leading to the formation of a more homogeneous reaction mass.

This improved dispersion enhances mass transfer and contributes to accelerated saponification under milder processing conditions.

Calculations of the apparent activation energy showed that when the soapstock is processed under the ultrasonic method, it is 1.2 times less compared to the classical one. This can be explained by the action of ultrasound with a relatively high intensity, which in turn reduces the size of the emulsion molecules. With the equation of the Arrhenius reaction rate constant, it was shown that the ultrasonic wave effectively increased the saponification extent, characterizing directly the increase in product yield.

While the laboratory results demonstrate that ultrasonic treatment accelerates soapstock saponification, industrial scalability depends on equipment design, energy efficiency, and reactor volume. Ultrasonic reactors for large-scale applications have been successfully implemented in the food, chemical, and biodiesel industries, where energy input and sonotrode configuration are optimized to maintain cavitation efficiency. Although scale-up may require higher power and appropriate mixing to ensure uniform sonication, the underlying kinetics and reaction enhancement observed at the lab scale are expected to translate to industrial settings with careful engineering considerations.

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