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High-Performance NAF Emulsifier Derived from Sustainable TOFA and Non-TOFA Sources

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Abstract

Recent disruptions in the supply chain for oilfield chemicals, combined with dynamic raw material availability and pricing highlighted the need to improve our flexibility in the production of drilling fluid additives. In this paper, we have broadly explored the chemistry of tall oil fatty acid (TOFA) and non-TOFA raw material sources to produce emulsifiers for non-aqueous drilling fluid (NAF). We used the design of experiments (DOE) to establish the boundaries of suitable non-TOFA, and introduced a new non-TOFA-based emulsifier. By applying experimental modeling, we demonstrate how the variability of raw materials and product manufacturing can be controlled to deliver consistency in performance.

Introduction

In the current business climate with a strong emphasis on sustainability and reduction of CO_2 footprint in the oil and gas industry, several high-profile initiatives have been launched to minimize our environmental impact. Specifically, for drilling and well construction activities, one such initiative is to increase the utilization of water-based drilling fluids (WBM) instead of synthetic-based mud (SBM) or non-aqueous drilling fluids. With ongoing investments, significant progress is expected to close the gap in performance between WBM and NAF. However, transitioning from NAF to WBM will necessitate a phased and gradual approach. In the meantime, NAF remains widely used due to their advantages over WBM, such as superior lubricity, desired fluid-shale interaction, and higher tolerance to contamination. Given that a substantial portion of wells are still drilled with NAF, technological advancements in NAF can significantly contribute to the immediate reduction of CO_2 emissions in drilling operations.

Extensive research has been conducted on novel emulsifiers for NAF. However, amidoamine-based emulsifiers synthesized with fatty acids, diethylenetriamine, and maleic anhydride continue to dominate the market despite the substantial volume of published studies. Such predominance may be attributed to their strong environmental compatibility, exceptional performance, and the global availability of raw materials. Our prior work has included the exploration of innovative emulsifiers (Khramov et al., 2023). However, economic and performance considerations ultimately guided us toward optimizing the chemistry of existing amidoamines rather than pursuing novel chemistries.

Despite over 30 years of commercial amidoamine production, our work (Khramov et al., 2020a; 2022) uncovered previously unrecognized aspects of this chemistry, advancing the understanding and optimization of these compounds. We identified key production refinements that enhance amidoamine performance. This progress was achieved by internalizing chemistry development and leveraging synergies between advanced chemical research and a comprehensive understanding of NAF.

The use of tall oil fatty acid, a key and long-established raw material derived from pine trees for amidoamine-based emulsifier production, has recently encountered significant challenges with its unstable availability and pricing. TOFA is a co-product of the pulp and paper industry. However, since TOFA is derived solely from fresh trees, ongoing improvements in paper recycling and the reduced demand for new paper may continue to impact its availability. This supply instability leads to price volatility. Such instability can lead to increased operational costs and supply chain disruptions. To enhance flexibility in drilling fluid additive production and to reduce our carbon footprint, we developed a concept that utilizes locally sourced raw materials for emulsifier manufacturing. This initiative, which offers the potential to lower environmental impact and transportation costs, supports our global decarbonization strategy in well-construction activities. However, this goal can only be realized if emulsifiers produced from local materials meet the required performance standards.

In this paper, we extended the discussion of amidoamine chemistry by examining the impact of alternative raw materials, specifically non-TOFA from various natural sources, on the performance of the NAF emulsifier. First, we provided a list of alternative fatty acids, considering their cost and availability, and conducted an initial evaluation of their properties. Next, a series of emulsifiers were synthesized using synthetic fatty acids with tailored saturation profiles designed to reflect the distribution found in natural sources. Performance-based testing was carried out, and key performance indicators (KPIs) were measured to establish a structure-activity relationship. To validate our findings, emulsifiers synthesized with commercially available fatty acids with a known saturation profile were tested again, yielding consistent results. Finally, field results utilizing properly made emulsifiers were presented, highlighting the significance of our findings.

Problem Statement

The substitution of TOFA with vegetable-sourced fatty acids (non-TOFA) is often perceived as compromising performance, with concerns that non-TOFA may not deliver equivalent results. However, given the wide variety of non-TOFA fatty acid sources, it is challenging to define the limitations of this raw material substitution, if any exist.

Methodology

Design-Expert software (Stat-Ease®) was employed to conduct the DOE and data analysis in this study. Our previous studies (Khramov et al., 2020a; 2020b; 2024) have highlighted the exceptional effectiveness of this approach in analyzing drilling fluid performance. By isolating meaningful data from background noise, evaluating measurement uncertainties, and establishing reliable trends across diverse conditions, this technique has proven to be an invaluable tool for achieving accurate and consistent results. A predictive model for each KPI was developed based on advanced statistics algorithms for performance prediction and raw material evaluation.

For the performance-based testing conducted in this work, a standard hot roll time (16 hours) was applied, with rheology measurements taken after hot roll at typical temperatures (40°F and 150°F). The hot roll temperature, HPHT fluid loss test temperature, or other changes made for specific experiments will be addressed in the following section.

Results and Discussion

Non-TOFA Sources

Common commercially available non-TOFAs and their saturation profile are shown in Figure 1. The saturation profile of TOFA is also included for reference. Through our extensive communication with fatty acid suppliers and comprehensive literature review, we identified that the primary difference between fatty acids derived from various vegetable sources lies in their saturation profile. It is important to note that, despite seasonal and geographical variations, TOFA consistently contains rosin (Magee and Zinkel, 1994), while fatty acids from vegetable oils do not. Based on our investigation and literature (Fleisher et al., 2013), we conclude that under typical reaction conditions used to produce amidoamines, rosins are unreactive and should be considered impurities. Therefore, for a fair comparison, distilled TOFA with minimized rosin content was used in this figure.

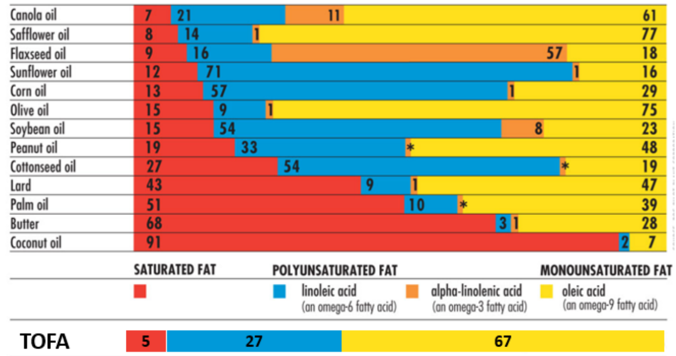

Figure 1— Saturation Profile of Non-TOFAs & TOFA (Reproduced from United States Department of Agriculture).

DOE with Synthetic Fatty Acid Blends

To better understand the impact of the saturation profile of different fatty acids on emulsifier performance in NAF, a DOE methodology was implemented. The experimental parameters used in this DOE are shown in Table 1. Synthetic fatty acids blended from palmitic acid (C_{16} saturated acid), oleic acid (C_{18} unsaturated fatty acid), and linoleic acid (C_{18} fatty acid with a higher level of unsaturation than oleic acid) were used for amidoamine emulsifier synthesis to achieve better control over the fatty acid saturation profile. The ranges of oleic and linoleic acids were selected based on the saturation profiles of natural sources (Figure 1). In our preliminary studies, we found that a higher ratio of saturated fatty acids in non-TOFA leads to undesirably high viscosity in both the emulsifiers and the formulated drilling fluids. Therefore, the highest concentration of saturated fatty acid (palmitic acid) in this study was limited to 25% to accommodate peanut oil and cottonseed oil (Figure 1). Palm oil (with 51% saturated acid) and coconut oil (91% saturated acid) were not considered for this study, as the saturated acid in these oils consists primarily of lauric acid (C_{12} saturated fatty acid) rather than palmitic acid (C_{16} saturated fatty acid). Our study also indicates that lauric acid has an even more detrimental effect on emulsifier and drilling fluid rheology, leading to the exclusion of these two oils from our DOE. A total of 24 different synthetic fatty acid blends were prepared and tested.

Table 1—Experimental Parameters in DOE

Parameters	Concentration
Palmitic Acid	0-25% in Synthetic Blend
Oleic Acid	40-100% in Synthetic Blend
Linoleic Acid	0-60% in Synthetic Blend
Emulsifier Loading	5-12 ppb in NAF

Emulsifier loadings in NAF, ranging from 5 to 12 ppb, were applied in the performance-based tests. Varying the emulsifier concentration ensures that switching from TOFA to non-TOFA sources does not result in increased product usage, thereby avoiding any adverse impact on the environmental footprint and carbon emissions associated with drilling fluids. While it is common industry practice to use 8 to 12 ppb of primary emulsifier in NAF lab testing, the lowest limit of emulsifier loading in this DOE was set to 5 ppb. In our previous work, (Khramov et al., 2020b), we demonstrated that high emulsifier dosages in NAF formulation tend to mask the performance difference between properly made and substandard emulsifiers, making product differentiation more difficult. Testing at lower concentrations also better simulates conditions where emulsifier depletion occurs in the field.

For emulsifier synthesis, we utilized a previously developed procedure in conjunction with automated lab synthesis equipment to ensure consistent performance. Significant time and effort were dedicated to optimizing this procedure to guarantee that the emulsifiers were manufactured correctly and reliably. These optimizations were critical to ensuring that the properly synthesized emulsifiers consistently delivered robust and repeatable performance, even when produced at different times, locations, or with varying raw material sources.

NAF were formulated, and their performance were evaluated according to API procedures. The formulation details of the NAF used to test the emulsifiers are provided in Table 2, while KPIs for NAF performance are shown in Table 3. Typical NAF properties such as 40°F rheology, 150°F rheology, and fluid loss were measured to develop a structure-activity correlation, followed by validation of the model using commercially available fatty acids in the next subsection.

Table 2— NAF Formulation Used in DOE

Component	Concentration (ppb)
Base Oil	134.0
Emulsifier	5.0-12.0
Wetting Agent	1.1
Rheology Modifier 1	3.5
Lime	5.0
25% $CaCl_2$ Brine	76.8
Organoclay	0.5
Fluid Loss Control Agent	0.2
Rheology Modifier 2	12.0
Rheology Modifier 3	2.0
Barite	354.0
SWR	77.0%
Volume	350 mL
MW	14.3 ppg

Table 3—KPIs in DOE

NAF KPIs	R600 at 40°F and 150°F
	R6 at 40°F and 150°F
	10-min Gel at 40°F and 150°F
	30 min Fluid Loss on Paper
Emulsifier KPIs	Acid number
	Amine number

DOE analysis indicates that the saturation profile (within the range shown in Table 1) of the synthetic fatty acids has a very minor impact on emulsifier KPIs (acid and amine number of the emulsifier), 150°F rheology, 10-min gel, and HPHT fluid loss (all below 4.5 mL). These results suggest that all the properly synthesized emulsifiers applied in this DOE can provide robust emulsion stability. Furthermore, the model demonstrates that emulsifier loadings ranging from 5 to 12 ppb have a minimal impact on HPHT fluid loss. This highlights the potential for reducing emulsifier dosage from the typical 8-12 ppb, provided the emulsifier is manufactured properly.

The major difference observed is the cold temperature NAF viscosity. While the ratio of oleic and linoleic acid has a minor impact on 40°F rheology, an increase in saturation content (palmitic acid ratio) will bring up cold temperature rheology. As shown in Figure 2(a), When emulsifier loading is at 5 ppb, R600 at 40°F increases from 220 to 250 when palmitic acid ratio increases from 0% to 25%. A similar, 14% increase in 40°F rheology can also be observed when the emulsifier loading is at 12 ppb (Figure 2(b)). Such an increase in cold rheology may be attributed to the higher crystallization tendency of saturated fatty acid molecules.

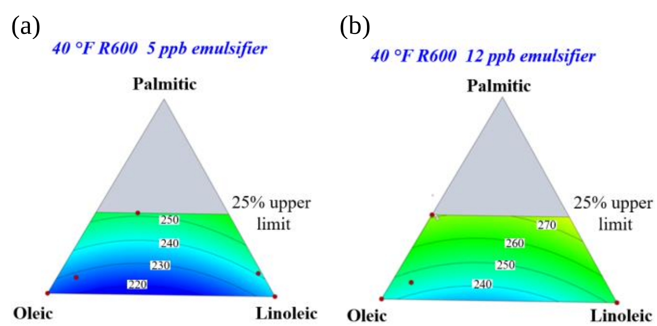

Figure 2—Statistic models created by the DOE tool: (a) R600 at 40°F with 5 ppb of emulsifier (b) R600 at 40°F with 12 ppb of emulsifier.

An increase in emulsifier dosage from 5 to 12 ppb was observed to result in higher cold rheology, rising from approximately 220–250 to 240–270. Since emulsifier dosage within this range has a minimal impact on fluid loss, lower dosages of high-quality, properly synthesized emulsifiers can be employed, thereby minimizing the effects of increased cold rheology. In contrast, poorly manufactured emulsifiers require higher loadings in NAF, which can negatively affect rheology and diminish the advantages of utilizing alternative raw materials such as non-TOFA.

Laboratory Validation with Commercial Non-TOFA

To validate the impact of fatty acid saturation profiles on the performance discussed earlier, emulsifiers were synthesized using two commercially available non-TOFA. The saturation profiles of these fatty acids are shown in Table 4, while the NAF formulation used for validation is detailed in Table 5. Performance-based testing results with the two commercial non-TOFA are provided in Table 6, with the results conducted with a commercially available TOFA emulsifier included for reference. The tests were performed in high-density fluid at 325°F to evaluate emulsifier capability under demanding conditions. The results indicate that both 40°F and 150°F rheology are similar among all three emulsifiers, while the two non-TOFA products demonstrate lower (better) HPHT fluid loss. However, this improvement is most likely attributed to the optimized manufacturing process for the non-TOFA emulsifiers rather than differences in the fatty acids themselves.

Notably, this example highlights the similarity in cold-temperature rheology. The 14% increase in rheology observed in results from increasing the saturated content from 0% to 25%, whereas the saturated content in most common vegetable oils (excluding palm and coconut oils) is relatively consistent, as shown in Figure 1.

Table 4—Saturation Profile of Two Commercially Available Non-TOFA

	Non-TOFA 1	Non-TOFA 2
Saturated	9.0	16.7
Oleic	63.0	20.1
Linoleic	28.0	63.2

Table 5—NAF Formulation Used to Compare Commercial Fatty Acids

Component	Concentration (ppb)
Base Oil	141.0
Emulsifier	7.0
Wetting Agent	1.1
Rheology Modifier 1	3.5
Lime	5.0
25% $CaCl_2$ Brine	77.6
Organoclay	0.5
Fluid Loss Control Agent	0.2
Rheology Modifier 2	12.0
Rheology Modifier 3	2.0
Barite	352.0
SWR	77.0%
Volume	350 mL
MW	14.3 ppg

Table 6—Performance of NAF with Emulsifiers Made by Non-TOFA and Commercial TOFA Emulsifier

	Commercial TOFA Emulsifier		Emulsifier Made by Non-TOFA 1		Emulsifier Made by Non-TOFA 2	
Heat Aging Temp, °F	325		325		325	
Heat Aging, hr	16		16		16	
Static/Rolling	D		D		D	
Mud Weight, lb/gal	14.3		14.3		14.3	
Rheology Temp, °F	**40**	**150**	**40**	**150**	**40**	**150**
R600, °VG	223	80	226	80	226	80
R300, °VG	123	44	126	45	123	48
R200, °VG	88	33	90	33	87	36
R100, °VG	49	23	51	22	48	24
R6, °VG	8	14	8	12	7	15
R3, °VG	7	12	6	12	5	17
PV, cP	100	36	100	35	103	32
YP, lb/100ft²	23	8	26	10	20	16
LSYP, lb/100ft²	6	11	4	12	3	19
10-sec Gel, lb/100ft²	10	18	7	19	6	19
10-min Gel, lb/100ft²	13	48	22	51	16	55
HTHP Temp, °F		325		325		325
HTHP FL, ml		7.4		4.2		5.2
Water in Filtrate, ml		0		0		0

Laboratory Validation of Toll-Manufactured Non-TOFA Emulsifier for Field Operation

Additional testing was conducted to evaluate the emulsifiers' suitability for applications in U.S. Land operations targeting the Haynesville formation, with the mud formulations listed in Table 7. The muds were hot rolled at 400°F for 16 hours, and HPHT fluid loss tests were conducted at 350°F. Only 150°F rheology was measured for this set of tests. It is noteworthy that, for this comparison, a non-TOFA emulsifier produced by our toll manufacturing partner was used instead of the lab-synthesized emulsifier referenced in the earlier sections.

Performance-based testing results are presented in Table 8. It can be observed that the 150°F rheology of the toll-manufactured non-TOFA emulsifier is comparable to that of the commercial TOFA emulsifier. However, the fluid loss results show significant improvement when using emulsifiers produced from non-TOFA sources. Consistent with the observations in Table 5, such an enhancement is attributed to the improved manufacturing process of the emulsifier rather than differences in the raw material composition used in its production.

Table 7—NAF Formulation for Haynesville Formation

Component	Concentration (ppb)
Base Oil	138.0
Emulsifier	8.0
Wetting Agent	2.0
Rheology Modifier 1	2.0
Lime	5.0
25% $CaCl_2$ Brine	46.0
Organoclay	6.0
Fluid Loss Control Agent	6.0
Rheology Modifier 2	1.2
Barite	458.0
SWR	85.0%
Volume	350 mL
MW	16.0 ppg

Table 8—Rheology and HPHT Fluid Loss (30-min on Paper) for Haynesville Formation

	Toll Manufactured Non-TOFA Emulsifier	Commercial TOFA Emulsifier
Heat Aging Temp, °F	400	400
Heat Aging, hr	16	16
Static/Rolling	D	D
Rheology Temp, °F	**150**	**150**
R600, °VG	102	124
R300, °VG	58	70
R200, °VG	41	50
R100, °VG	23	29
R6, °VG	4	6
R3, °VG	4	5
PV, cP	44	54
YP, lb/100ft²	14	16
LSYP, lb/100ft²	4	4
10-sec Gel, lb/100ft²	5	23
10-min Gel, lb/100ft²	14	24
HTHP Temp, °F	350	350
HTHP FL, ml	5.0	80.0
Water in Filtrate, ml	0.0	0.0

The results of these laboratory investigations suggest that TOFA- and non-TOFA-based emulsifiers can deliver largely equivalent performance, enabling the interchangeable use of different raw materials without compromising quality. This flexibility allows for better adaptability to market dynamics, fluctuations in raw material availability, and regional variations in sourcing. Moreover, local sourcing and manufacturing can significantly reduce the carbon footprint, thereby enhancing sustainability. Most importantly, the key determinant of emulsifier performance is the precision and reliability of the manufacturing process. Consistency and high performance are driven more by proper production techniques than by the specific raw materials used.

Field Results by Properly Made Emulsifiers

Based on the findings presented in this paper, we expect that emulsifiers produced from non-TOFA will exhibit comparable performance in similar challenging environments. In our experience, when an emulsifier is manufactured correctly, its performance in the field is consistently exceptional. The following example presents a representative case of NAF performance in U.S. Land operations, once again highlighting the critical role of precision and reliability in the manufacturing process.

A properly made amidoamine emulsifier was used in the Haynesville formation of North-Western Louisiana and Eastern Texas, and it demonstrated its exceptional performance when used at optimal concentrations. The emulsifier provided stable fluid properties, including rheology, formation stability control, and lubricity, enabling smooth operations under challenging downhole conditions. These conditions include bottom-hole circulating temperatures consistently exceeding 350°F, occasionally surpassing 400°F, in conjunction with bottom-hole pressures ranging from 10,000 to 15,000 psi. The emulsifier chemistry proved effective across various base oils, such as red dye diesel, low toxicity mineral oils (LTMO) like EDC170SE, and synthetic paraffin-based fluids such as NEOFLO 4633. This successful operation showcases the versatility and reliability of properly made emulsifiers under extreme operating environments.

In addition to the success in the Haynesville formation, a recent adoption of the properly made emulsifier in the Marcellus Shale, located in Southwestern Pennsylvania has delivered immediate enhancements to operator drilling performance. This has resulted in record-setting 24-hour footage rates without compromising NAF's rheology or emulsion stability. This success further demonstrates the effectiveness and adaptability of a properly made emulsifier in diverse operational environments.

Conclusions

Fatty acids from non-TOFA sources, primarily composed of C_{18} fatty acids with less than 25% saturated fatty acids, are excellent alternatives to TOFA for the production of high-performance amidoamine-based NAF emulsifiers. This finding was validated through a series of performance-based tests on synthetic fatty acids, utilizing advanced statistical tools, and further confirmed by testing on commercial non-TOFA emulsifiers. Fatty acid source has minimal impact on important emulsifier and NAF KPIs such as HPHT fluid loss, acid number, amine number, and 150°F rheology. An increase in the saturation content of fatty acids leads to a rise in 40°F rheology. Such an increase in cold temperature rheology can be attributed to the higher crystallization tendency of saturated fatty acid molecules. Therefore, vegetable oils with high C_8-C_{18} saturated fatty acids, such as coconut or palm oil, are not suitable raw materials for amidoamine emulsifier production. Additionally, it is worth noting that rosin acids present in TOFA neither contribute any tangible benefit to emulsifier quality or performance testing and could be considered impurities.

The most critical technical factor in producing amidoamine emulsifiers, whether using TOFA or non-TOFA, is ensuring the correct execution of the synthesis process. Two field results in US Land demonstrated that the properly made emulsifiers showcased robust performance under harsh conditions (400°F, 10,000 to 15,000 psi) and are compatible with a wide variety of base oils such as diesel, LTMO, and synthetic paraffin.

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Nomenclature

DOE = Design of experiments
HPHT = High-pressure high-temperature
KPI = Key performance indicator
LTMO = Low toxicity mineral oil
NAF = Nonaqueous drilling fluids
SBM = Synthetic-based mud
TOFA = Tall oil fatty acid

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