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(54) Title: TUNING SULFONATION AND CONTROLLING OLEO-FURAN SURFACTANT COMPOSITIONS

(57) Abstract: Disclosed herein are methods for sulfonation of oleo-furan compounds derived from a furan moiety and either an individual fatty acid or a mixture of fatty acids representative of those yielded from one or more plant oils. Additionally, this disclosure describes tuning sulfonation conditions to produce oleo-furan sulfonate blends which can demonstrate beneficial surfactant characteristics and improvements in various applications.

TUNING SULFONATION AND CONTROLLING OLEO-FURAN SURFACTANT COMPOSITIONS

RELATED APPLICATIONS

[1] This disclosure claims priority to US provisional patent application number 63/288,256, filed on December 10, 2021, and US provisional patent application number 63/388,872, filed on July 13, 2022, the contents of each of these provisional applications being hereby incorporated by reference.

TECHNICAL FIELD

[2] This disclosure generally relates to surfactant compositions and related methods for synthesizing such surfactants. In particular, disclosed herein are embodiments including oleo-furan surfactant compositions and related methods for tuning sulfonation of oleo-furans and controlling oleo-furan surfactant compositions.

BACKGROUND

[3] Surfactants are chemical compounds that have a variety of applications. Such applications can include household cleaners and detergents, institutional & industrial cleaning products, agricultural chemicals such as spray adjuvants, oilfield applications, and various coating additives. Short for surface active agent, a surfactant consists of a hydrophilic moiety, which attracts water, and a hydrophobic moiety, which attracts oil and dirt. The amphiphilic structure of surfactant molecules enables them to suspend dirt, emulsify, and modify surface properties of materials. Variations in the chemical structure of a surfactant molecule can enable tunable properties, such as emulsifying capability (hydrophilic/lipophilic balance), oil/dirt suspension capacity (critical micelle concentration), cold water performance (Krafft point), hard water tolerance (stability to calcium and magnesium ions), different types of foaming including pour and high shear, level of skin irritation, color, and biodegradation.

[4] Commercially manufactured surfactants are generally synthesized entirely or in part from petrochemical feedstocks, such as long chain alkanes/alkenes and ethylene oxide. Emerging trends toward eco-friendly surfactants have shifted focus toward materials derived from renewable sources. Development has focused largely on replacing current petrochemical surfactants with bio-based analogues with identical chemical structure (e.g., sodium lauryl sulfate from petroleum and sodium coco sulfate from coconut oil).

[5] Despite decades of development, nearly all surfactant structures are faced by a unified problem: the presence of hard water (containing calcium, magnesium, iron, etc.) inactivates surfactants. Inactivation causes surfactants to form solid precipitates and substantially lose function. Development of a new class of bio-based surfactants, called oleo-furan surfactants (OFS), can overcome the hard water inactivation challenge associated with prior surfactant structures, demonstrating 50-100 times greater calcium tolerance compared with other surfactants.

SUMMARY

[6] Oleo-furan surfactants can be synthesized through a multi-step process involving hydrolysis of a triglyceride molecule to form fatty acids, dehydration of the fatty acids to form fatty acid anhydrides, and acylation of furan with a fatty acid anhydride. Subsequent steps can include optional reactions, such as reduction/hydrogenation of oxygen functionality or aldol condensation to incorporate chemical branched structures, as well as chemical modification of the furan moiety with sulfonates, sulfates, or other oxygen moieties to form a hydrophilic group. Between each reaction step there can be a purification step (e.g., distillation) to effectively separate out byproducts, solvents, and products.

[7] The present disclosure describes embodiments of methods for sulfonation of oleo-furan compounds derived from a furan moiety and either an individual fatty acid or a mixture of fatty acids representative of those yielded from plant oils (e.g., coconut oil). Additionally, this disclosure describes embodiments where tuning the sulfonation conditions produces new, unique oleo-furan sulfonate blends which can demonstrate beneficial surfactant characteristics and improvements in various applications. Finally, the synergistic effects of oleo-furan sulfonate blends and improvements on individual surfactant properties are described with reference to the methods that provide more optimal surfactant selectivity.

[8] The disclosed sulfonation method embodiments and the disclosed resulting surfactant mixture embodiments can be differentiated from previous oleo-furan surfactant synthesis processes because of a difference in chemical composition of these newly discovered surfactants as well as the expanded set of reaction conditions, including sulfonating agents, reagent loading, solvent selection, reaction temperature and reaction time that were tested for impact on surfactant preparation. Prior to the work that led to this disclosure, it was unknown that the position and number of sulfonate functional groups on the oleo-furan sulfonate surfactant molecules could be altered. As a result of the sulfonation techniques disclosed herein, method embodiments for precisely controlling the selectivity of oleo-furan

sulfonation reactions have been elucidated, which allows for tuning reaction conditions to achieve high selectivity to a specific sulfonation position and/or number, or to achieve a specific ratio of different sulfonation positions/numbers that can achieve superior functional properties compared to individual oleo-furan surfactants. The method embodiments detailed below that enable control over the number of sulfonate groups per surfactant molecule notably allow for controlled alteration of the hydrophilic-lipophilic balance of a surfactant to achieve superior application performance with variable carbon content.

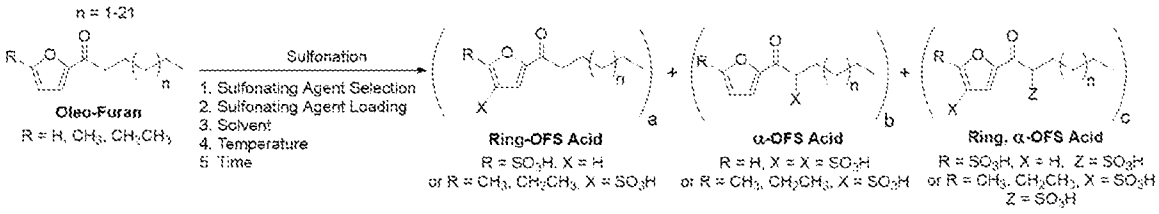
[9] The embodiments disclosed herein can be applied in the chemicals industry, including production of consumer products, such as detergents, cleaners, and personal care products. Surfactant production is relevant to manufacturers who produce bulk surfactants, as well as formulators, who generate consumer products containing surfactants. In particular, a subset of the disclosed surfactant class has properties similar or superior to the commercial surfactant sodium laureth sulfate, while avoiding the likely carcinogenic compound 1,4-dioxane produced as a byproduct of sodium laureth sulfate synthesis.

[10] Uses for surfactant compositions disclosed herein can include two primary product classes: (1) cleaning components, with formulations that include surfactants, builders, carriers, enzymes, alkalis, organic polymeric compounds, dyes/colorants, bleaches, alkanolamines, soil suspension agents, abrasives, fabric softening agents, fragrances, hydrotropes, opacifiers, preservatives, dispersants, processing aids, solvents, sud control agents, antimicrobial agents, anti-redeposition agents, and/or corrosion inhibitors, and (2) personal care products, with formulations that include surfactants, oils, emollients, moisturizers, carriers, extracts, vitamins, minerals, alkalis, anti-aging compounds, solvents, polymers, preservatives, antimicrobials, waxes, particles, colorants/dyes, abrasives, antimicrobial agents, opacifiers, processing aids, and/or fragrances.

[11] Cleaning component formulations incorporating one or more surfactant compositions disclosed herein can take the form of liquid detergents, such as laundry, dishwashing, and hand dishwashing detergents, solid detergents, including powders, bars, and tablets, as well as industrial cleaners, hard surface cleaners, disinfectants, and decontaminants. Personal care product formulations incorporating one or more surfactant compositions disclosed herein can take the form of hair shampoos, conditioners, and treatments, as well as body wash, lotion, facial and body soap, foam bath, make-up removers, skin care products, acne control products, shaving aids, deodorants, antiperspirants, cosmetics, depilatory, and fragrances. Additional applications for surfactant embodiments disclosed herein can include agricultural chemicals (e.g., spray adjuvants, emulsifiers for pesticides/herbicides, spray tank additives,

and drift reducers), oilfield applications (e.g., enhanced oil recovery, oil spill remediation), and paints/inks/coatings (e.g., emulsifiers, pigment stabilizers).

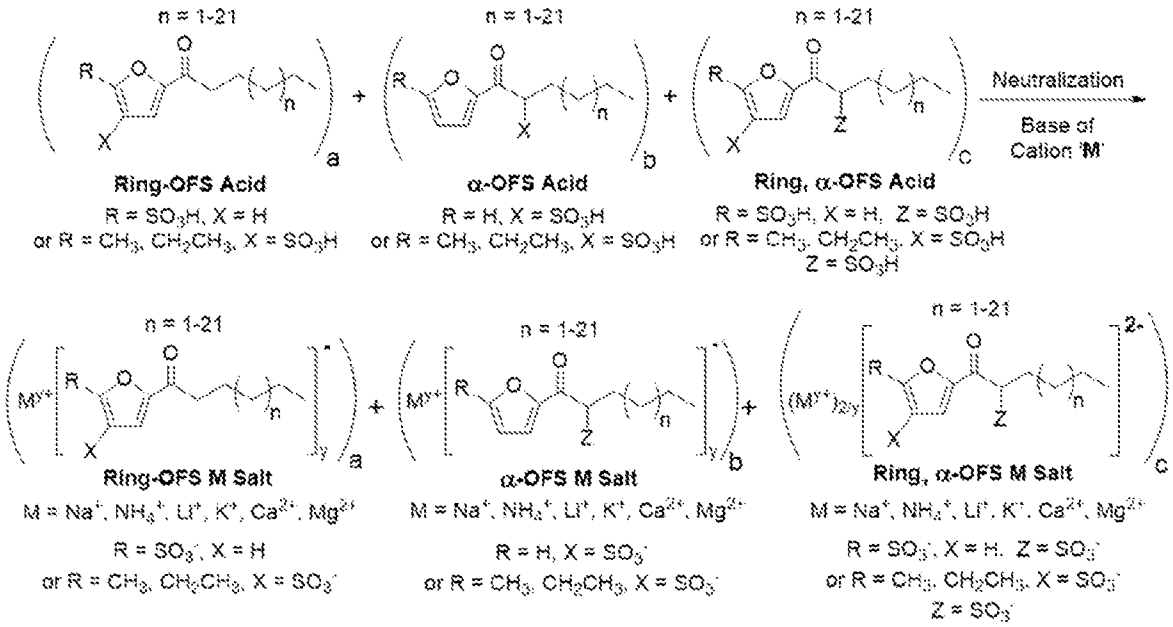
[12] One exemplary embodiment includes a method of sulfonating an oleo-furan (OF) molecule or substituted oleo-furan molecule (e.g., oleo-methylfuran, OMF) via the following reaction scheme, Scheme 1:



Scheme 1

[13] Scheme 1 illustrates sulfonation of oleo-furans to produce oleo-furan sulfonic acids with mole ratios a, b, and c, where tuning of noted reaction parameters 1-5 (sulfonating agent selection, sulfonating agent loading, solvent, temperature, and time) can be used to achieve controlled selectivity for different mole ratios of the compounds shown. Namely, various combinations of (1) sulfonating agent, (2) sulfonating agent loading, indicated by the molar ratio of sulfonating agent to oleo-furan added to the reaction mixture, (3) solvent used or absence thereof (neat), (4) temperature and (5) reaction time can provide selective formation of one or more oleo-furan sulfonic acids. Optional neutralization of the formed sulfonic acids with a base as illustrated in Scheme 2, below, can yield surfactant salts of General Structure 1 (GS1), illustrated below. Schemes 1 and 2 illustrate the general sulfonation and neutralization processes that may utilize a number of oleo-furan feedstocks, including those with ring-substituted functional groups such as -H, $-CH_3$, $-CH_2CH_3$, a longer alkyl chain, -OH, $-SO_3$-, $-SO_3H$, or other functional groups, and 'n' designates a variable number of carbon atoms (n = 1-21) that are part of an extended saturated or unsaturated alkyl chain with a total of 6-26 carbons in length, where the alkyl chain includes the carbon atom connected to the furan ring with an acyl group.

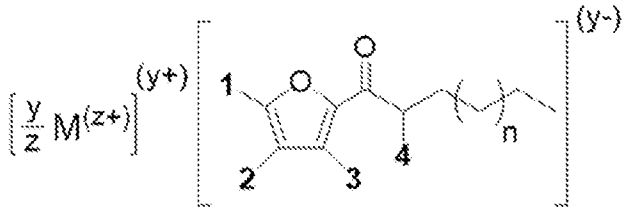
[14] As noted, another exemplary embodiment includes a method that includes neutralization of oleo-furan sulfonic acids via the following exemplary reaction scheme, Scheme 2:



Scheme 2

[15] Scheme 2 illustrates neutralization of oleo-furan sulfonic acids with mole ratios a, b, and c, where the product mole ratios of each surfactant can be identical to those for the corresponding sulfonic acid precursors, and the cation (M) is the cation(s) matching the base used during the neutralization process.

[16] Methods disclosed herein can be carried out to produce various compound embodiments. One such exemplary embodiment includes a compound having the formula (General Structure 1 or "GS1"):



General Structure 1

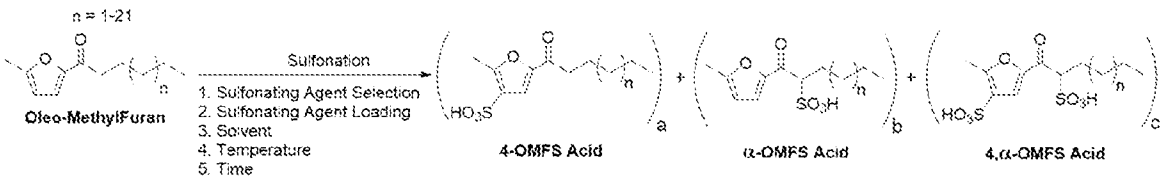
[17] For General Structure 1, the position of the sulfonate moiety either on the oleo-furan ring (Ring-OFS), the alkyl chain adjacent to the ketone functional group (α-OFS) or in both positions (Ring, α-oleo-furan disulfonate) can be controlled by the reaction parameters including (1) sulfonating reagent, (2) sulfonating reagent loading, (3) solvent, (4) temperature, and (5) reaction time. Each numbered position in General Structure 1 designates a functional group, such as -H, $-CH_3$, a longer alkyl chain, $-SO_3^-$, or other functional group, with at minimum one of the functional groups 1-4 comprising a sulfonate (SO_3^-) functional group, and 'n' designating a variable number of carbon atoms (n = 1-21) that are part of an

extended saturated or unsaturated alkyl chain with a total of 6-26 carbons in length, where the alkyl chain includes the carbon atom connected to the furan ring with an acyl group. In some embodiments of General Structure 1, if either position 1 or 2 is a sulfonate ($-SO_3^-$), a second sulfonate functional group is present in position 4.

[18] A more specific method embodiment of Scheme 1 disclosed herein includes Scheme 3, which can start with an oleo-methylfuran (OMF) compound and use a particular combination of the reaction parameters 1-5 to produce oleo-methylfuran sulfonic acids (OMFS Acid) with defined selectivity for a reproducible molar ratio of products a, b and c representing 4-OMFS Acid (a ring sulfonation in the 4th ring position, or location 2 in General Structure 1), α-OMFS Acid, and 4, α-OMFS Acid. In a further embodiment, subsequent neutralization of these sulfonic acids according to the general method shown in Scheme 2 can be seen below as the exemplary Scheme 4, which can result in the OMFS surfactant salts with the cation matching the base used during neutralization, such as sodium, ammonium, lithium, potassium, calcium and magnesium, and molar ratios a, b and c for each product matching the sulfonic acid.

[19] The exemplary embodiment of the sulfonation method shown in Scheme 5 uses an oleo-methylfuran feedstock with a C_{12} alkoyl saturated carbon chain derived from lauric acid, dodecanoylmethylfuran, and provides a mechanism and rate constants for formation of each oleo-furan sulfonic acid produced during sulfonation of dodecanoylmethylfuran. In some embodiments, surfactants can be derived from oleo-furans prepared from a distribution of fatty acids with varying alkyl chain length and varying degrees of unsaturation, such as those obtained from soybean oil, to produce surfactant mixtures of varying alkyl chain length, the final product of which may or may not contain chain unsaturation.

[20] As noted, another embodiment includes a method that utilizes a disubstituted furan to produce oleo-methylfuran sulfonic acids via the following exemplary reaction scheme, Scheme 3:

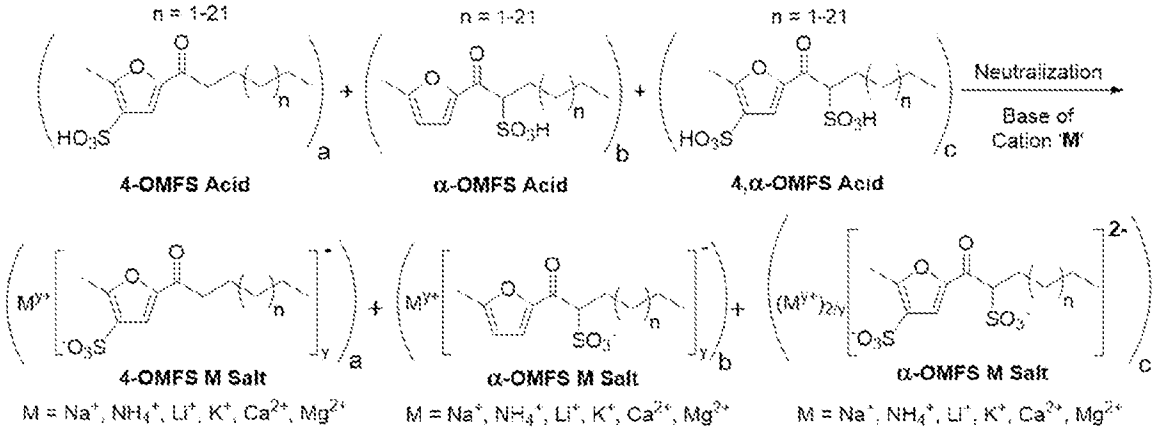


Scheme 3

[21] Scheme 3 illustrates oleo-furan sulfonation method using a disubstituted furan to produce oleo-methylfuran sulfonic acids with mole ratios a, b, and c, where tuning of reaction

parameters 1-5 can used to achieve controlled selectivity for different mole ratios of the sulfonic acid products shown.

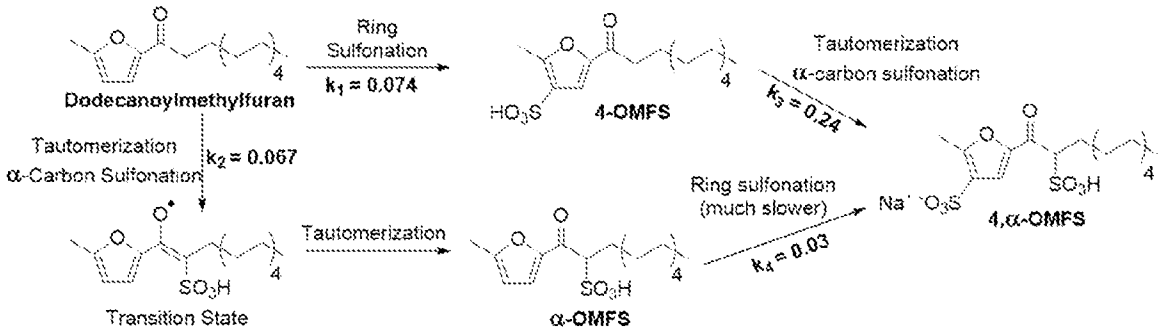
[22] As also noted, an additional embodiment includes a method that includes an oleo-furan sulfonic acid neutralization process to produce oleo-methylfuran sulfonate surfactant salts via the following exemplary reaction scheme, Scheme 4:



Scheme 4

[23] Scheme 4 illustrates an oleo-furan sulfonic acid neutralization process to produce oleo-methylfuran sulfonate surfactant salts with mole ratios a, b, and c, with adjustment of surfactant cation controlled by selection of base used in the neutralization process.

[24] Finally, as also noted, another embodiment includes a method that includes sulfonation of dodecanoylmethylfuran with sulfuric acid sulfonating agent via the following exemplary reaction scheme, Scheme 5:

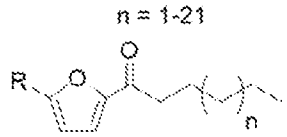


Scheme 5

[25] Scheme 5 illustrates reaction mapping and rate constants for the sulfonation of dodecanoylmethylfuran with sulfuric acid sulfonating agent (with mole ratios sulfuric acid: dodecanoylmethylfuran in the range from 1:1 to 3.8:1) using acetonitrile solvent in a temperature range between 40°C and 50°C. The mechanism is shown for formation of ring (4-OMFS) and chain (α-OMFS) monosulfonic acids as well as a combined disulfonic acid

product (4,α-OMFS) formed from a secondary sulfonation of either the ring or α monosulfonic acids.

[26] Another embodiment includes a method. This method embodiment includes providing an oleo-furan compound according to the formula (1):

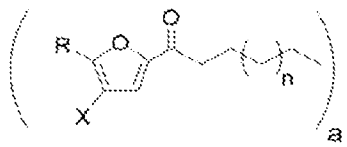


Oleo-Furan

R = H, CH_3, CH_2CH_3

(1).

And, this method includes sulfonating this provided oleo-furan compound to produce at least two of a first oleo-furan sulfonic acid according to formula (2), a second oleo-furan sulfonic acid according to formula (3), and a third oleo-furan sulfonic acid according to formula (4):

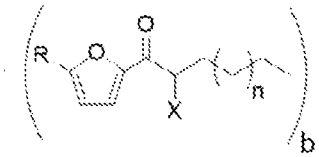


Ring-OFS Acid

R = SO_3H, X = H

or R = CH_3, CH_2CH_3, X = SO_3H

(2),

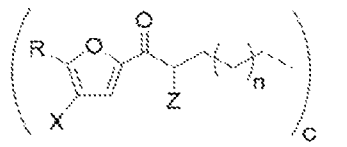


α-OFS Acid

R = H, X = SO_3H

or R = CH_3, CH_2CH_3, X = SO_3

(3),



Ring, α-OFS Acid

R = SO_3H, X = H, Z = SO_3H

or R = CH_3, CH_2CH_3, X = SO_3H

Z = SO_3H

(4),

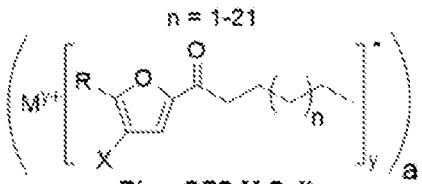
In the above formulas, n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and a, b, and c represent mole ratios of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

[27] In a further embodiment of this method, sulfonating the provided oleo-furan compound can include sulfonating the provided oleo-furan compound to produce each of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

[28] In a further embodiment of this method, the method additionally includes selecting a sulfonating agent to control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). As one such example, selecting the sulfonating agent can include selecting a first sulfonating agent to produce a first mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). It can also include selecting a second sulfonating agent to produce a second mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4), and where the second sulfonating agent is different than the first sulfonating agent and the second mole ratio is different than the first mole ratio. As another such example, the method can further include selecting at least one of a sulfonating agent loading, a solvent type, a sulfonation temperature, and a sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). For instance, in this example, selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time can include selecting each of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). In another instance, selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time can include: selecting a first sulfonation temperature and a first

sulfonation reaction time to produce a first mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4); and selecting a second sulfonation temperature and a second sulfonation reaction time to produce a second mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4), where the second sulfonation temperature is different than the first sulfonation temperature, the second sulfonation reaction time is different than the first sulfonation reaction time, and the second mole ratio is different than the first mole ratio.

[29] In a further embodiment of this method, the method can additionally include neutralizing the produced at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4) to produce at least two of a first neutralized oleo-furan sulfonic acid according to formula (5), a second neutralized oleo-furan sulfonic acid according to formula (6), and a third neutralized oleo-furan sulfonic acid according to formula (7):



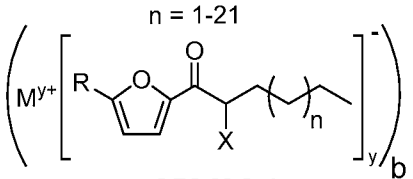
Ring-OFS M Salt

$M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}$

$R = SO_3^-, X = H$

or $R = CH_3, CH_2CH_3, X = SO_3^-$

(5),



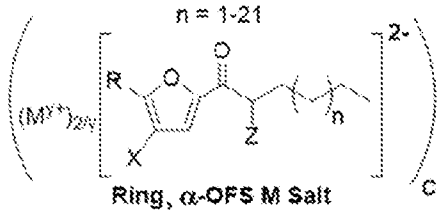
α-OFS M Salt

$M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}$

$R = H, X = SO_3^-$

or $R = CH_3, CH_2CH_3, X = SO_3^-$

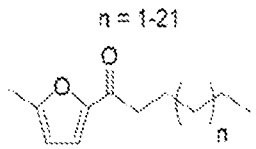
(6),



(7),

where a, b, and c represent mole ratios of the at least two of the first neutralized oleo-furan sulfonic acid according to formula (5), the second neutralized oleo-furan sulfonic acid according to formula (6), and the third neutralized oleo-furan sulfonic acid according to formula (7). As one such example, neutralizing the produced at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4) can include neutralizing each of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4) to produce each of the first neutralized oleo-furan sulfonic acid according to formula (5), the second neutralized oleo-furan sulfonic acid according to formula (6), and the third neutralized oleo-furan sulfonic acid according to formula (7).

[30] Another embodiment includes a method. This method embodiment includes providing an oleo-methylfuran compound according to the formula (1):

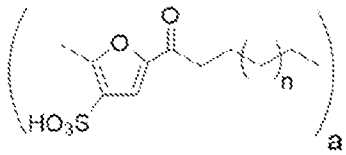


Oleo-MethylFuran

[31]

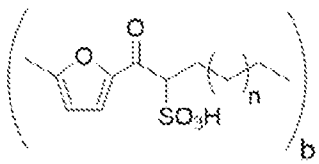
[32] (1); and

And, this method embodiment includes sulfonating [1] the provided oleo-methylfuran compound to produce at least two of a first oleo-methylfuran sulfonic acid according to formula (2), a second oleo-methylfuran sulfonic acid according to formula (3), and a third oleo-methylfuran sulfonic acid according to formula (4):



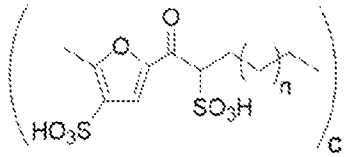
4-OMFS Acid

(2),



α-OMFS Acid

(3),



4,α-OMFS Acid

(4),

In the above formulas, n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and a, b, and c represent mole ratios of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

[33] In a further embodiment of this method, sulfonating the provided oleo-methylfuran compound can include sulfonating the provided oleo-methylfuran compound to produce each of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

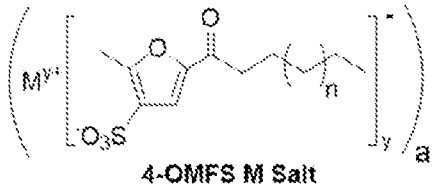
[34] In a further embodiment of this method, the method can additionally include selecting a sulfonating agent to control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4). As one such example, selecting the sulfonating agent can include selecting a first sulfonating agent to produce a first mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4). In this such example, selecting the sulfonating agent can further include

selecting a second sulfonating agent to produce a second mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4), where the second sulfonating agent is different than the first sulfonating agent and the second mole ratio is different than the first mole ratio.

[35] In a further embodiment of this method, the method can additionally include selecting at least one of a sulfonating agent loading, a solvent type, a sulfonation temperature, and a sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4). As one such example, selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time can include selecting each of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4). For instance, selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time can include: selecting a first sulfonation temperature and a first sulfonation reaction time to produce a first mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4), and selecting a second sulfonation temperature and a second sulfonation reaction time to produce a second mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4), where the second sulfonation temperature is different than the first sulfonation temperature, the second sulfonation reaction time is different than the first sulfonation reaction time, and the second mole ratio is different than the first mole ratio.

[36] In a further embodiment of this method, the method can additionally include neutralizing the produced at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) to produce at least two of a first neutralized oleo-methylfuran sulfonic acid according to formula (5), a second neutralized

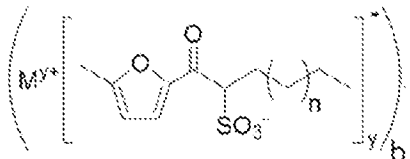
oleo-methylfuran sulfonic acid according to formula (6), and a third neutralized oleo-methylfuran sulfonic acid according to formula (7):



4-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

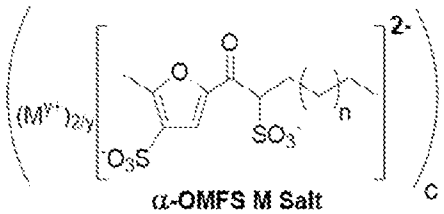
(5),



α-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

(6),



α-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

(7),

In the above formulas, a, b, and c represent mole ratios of the at least two of the first neutralized oleo-methylfuran sulfonic acid according to formula (5), the second neutralized oleo-methylfuran sulfonic acid according to formula (6), and the third neutralized oleo-methylfuran sulfonic acid according to formula (7). As one example, neutralizing the produced at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) can include neutralizing each of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) to produce each of the first neutralized oleo-methylfuran sulfonic acid according to formula (5), the second neutralized oleo-methylfuran sulfonic acid according to formula (6), and the third neutralized oleo-methylfuran sulfonic acid according to formula (7).

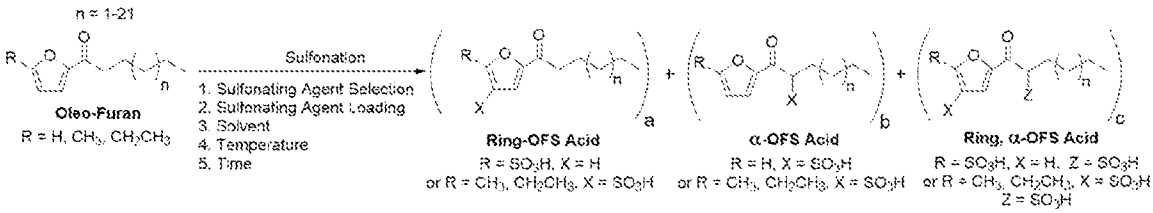
DETAILED DESCRIPTION

[37] The following detailed description is exemplary in nature and is not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the following description provides some practical illustrations for implementing exemplary embodiments of the present invention. Examples of elements, materials, compositions, and/or steps are provided below. Though those skilled in the art will recognize that many of the noted examples have a variety of suitable alternatives that are also within the scope of the present disclosure.

[38] Embodiments disclosed herein relate to surfactant compositions and related methods for synthesizing such surfactants. In particular, disclosed herein are embodiments including oleo-furan surfactant compositions and related methods for tuning sulfonation of oleo-furans and controlling oleo-furan surfactant compositions.

[39] More specifically, this disclosure embodiments of methods for sulfonation of oleo-furan compounds derived from a furan moiety and either an individual fatty acid or a mixture of fatty acids representative of those yielded from plant oils (e.g., coconut oil). Additionally, this disclosure describes embodiments where tuning the sulfonation conditions produces new, unique oleo-furan sulfonate blends which can demonstrate beneficial surfactant characteristics and improvements in various applications.

[40] One exemplary embodiment includes a method of sulfonating an oleo-furan (OF) molecule or substituted oleo-furan molecule (e.g., oleo-methylfuran, OMF) via the following reaction scheme, Scheme 1:

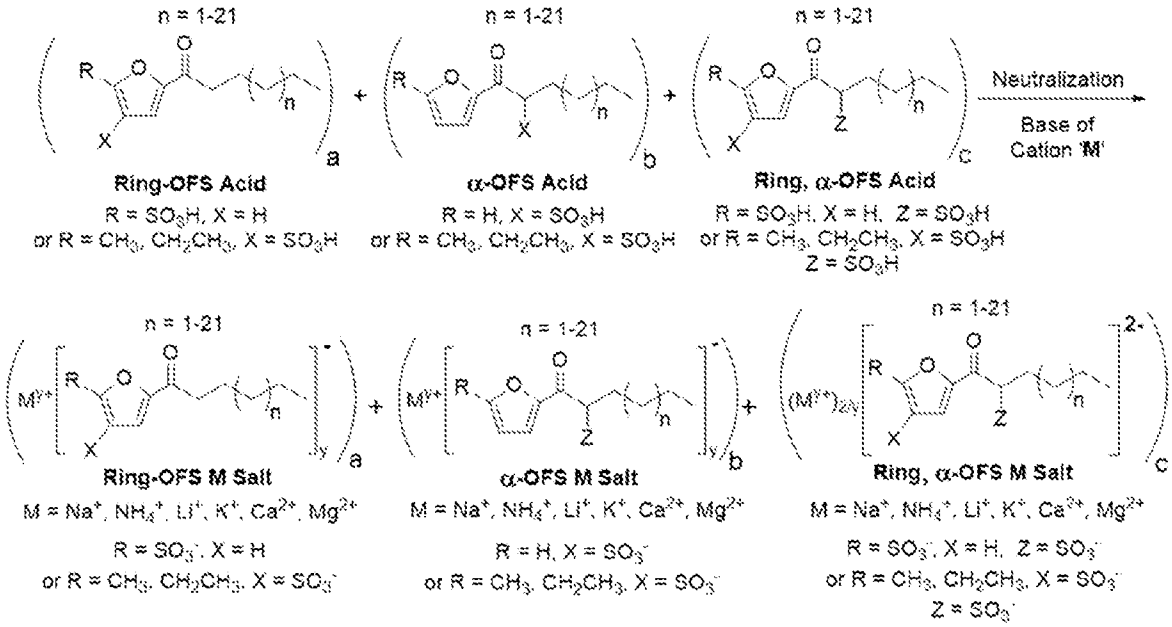


Scheme 1

[41] Scheme 1 illustrates sulfonation of oleo-furans to produce at least two of the three illustrated oleo-furan sulfonic acids with mole ratios a, b, and c, where tuning of noted reaction parameters 1-5 can used to achieve controlled selectivity for different mole ratios of the compounds shown. Namely, various combinations of (1) sulfonating agent, (2) sulfonating agent loading, indicated by the molar ratio of sulfonating agent to oleo-furan added to the reaction mixture, (3) solvent used or absence thereof (neat), (4) temperature and (5) reaction time can provide selective formation of one or more oleo-furan sulfonic acids.

Optional neutralization of the formed sulfonic acids with a base as illustrated in Scheme 2, below, can yield surfactant salts of General Structure 1 (GS1), illustrated below. Schemes 1 and 2 illustrate the general sulfonation and neutralization processes that may utilize a number of oleo-furan feedstocks, including those with ring-substituted functional groups such as -H, -CH_3, -CH_2CH_3, a longer alkyl chain, -OH, -SO_3-, -SO_3H, or other functional groups, and 'n' designates a variable number of carbon atoms (n = 1-21) that are part of an extended saturated or unsaturated alkyl chain with a total of 6-26 carbons in length, where the alkyl chain includes the carbon atom connected to the furan ring with an acyl group.

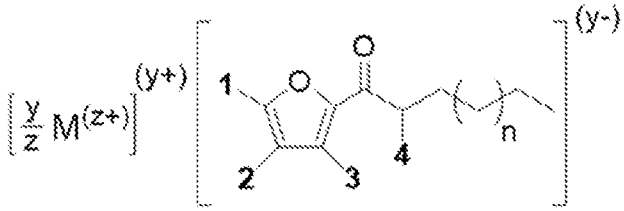
[42] As noted, another exemplary embodiment includes a method that includes neutralization of oleo-furan sulfonic acids via the following exemplary reaction scheme, Scheme 2:



Scheme 2

[43] Scheme 2 illustrates neutralization of oleo-furan sulfonic acids with mole ratios a, b, and c, where the product mole ratios of each surfactant can be identical to those for the corresponding sulfonic acid precursors, and the cation (M) is the cation(s) matching the base used during the neutralization process.

[44] Methods disclosed herein can be carried out to produce various compound embodiments. One such exemplary embodiment includes a compound having the formula General Structure 1 ("GS1") as follows:



General Structure 1

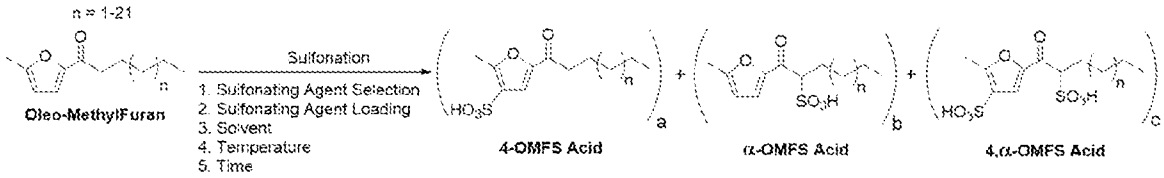
[45] For General Structure 1, the position of the sulfonate moiety either on the oleo-furan ring (Ring-OFS), the alkyl chain adjacent to the ketone functional group (α-OFS) or in both positions (Ring, α-oleo-furan disulfonate) can be controlled by the reaction parameters including (1) sulfonating reagent, (2) sulfonating reagent loading, (3) solvent, (4) temperature, and (5) reaction time. Each numbered position in General Structure 1 designates a functional group, such as -H, -CH_3, a longer alkyl chain, -SO_3-, or other functional group, with at minimum one of the functional groups 1-4 comprising a sulfonate (SO3-) functional group, and 'n' designating a variable number of carbon atoms (n = 1-21) that are part of an extended saturated or unsaturated alkyl chain with a total of 6-26 carbons in length, where the alkyl chain includes the carbon atom connected to the furan ring with an acyl group. In some embodiments of General Structure 1, if either position 1 or 2 is a sulfonate (-SO_3-), a second sulfonate functional group is present in position 4.

[46] A more specific method embodiment of Scheme 1 disclosed herein includes Scheme 3, which can start with an oleo-methylfuran (OMF) compound and use a particular combination of the reaction parameters 1-5 to produce oleo-methylfuran sulfonic acids (OMFS Acid) with defined selectivity for a reproducible molar ratio of products a, b and c representing 4-OMFS Acid (a ring sulfonation in the 4th ring position, or location 2 in General Structure 1), α-OMFS Acid, and 4, α-OMFS Acid. In a further embodiment, subsequent neutralization of these sulfonic acids according to the general method shown in Scheme 2 can be seen below as the exemplary Scheme 4, which can result in the OMFS surfactant salts with the cation matching the base used during neutralization, such as sodium, ammonium, lithium, potassium, calcium and magnesium, and molar ratios a, b and c for each product matching the sulfonic acid.

[47] The exemplary embodiment of the sulfonation method shown in Scheme 5 uses an oleo-methylfuran feedstock with a C_{12} alkoyl saturated carbon chain derived from lauric acid, dodecanoylmethylfuran, and provides a mechanism and rate constants for formation of each oleo-furan sulfonic acid produced during sulfonation of dodecanoylmethylfuran. In some embodiments, surfactants can be derived from oleo-furans prepared from a distribution of

fatty acids with varying alkyl chain length and varying degrees of unsaturation, such as those obtained from soybean oil, to produce surfactant mixtures of varying alkyl chain length, the final product of which may or may not contain chain unsaturation.

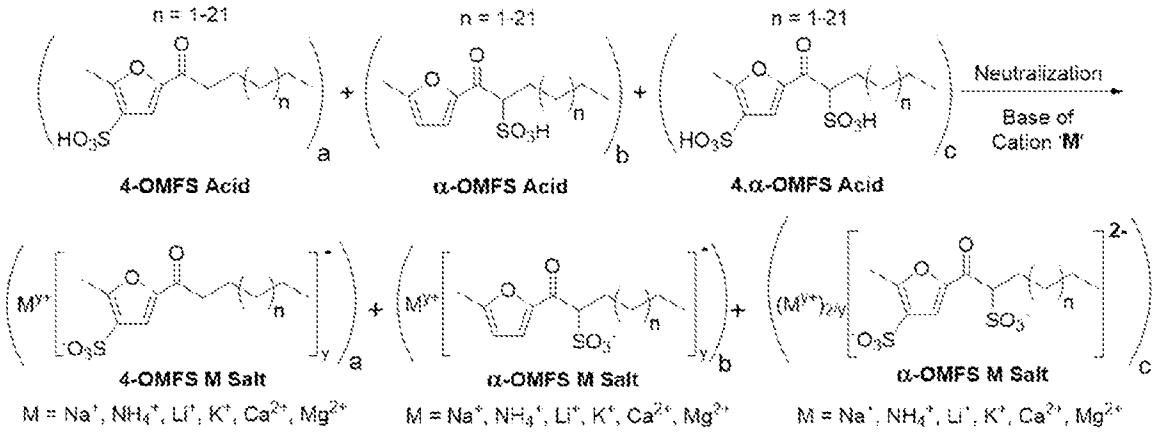
[48] As noted, another embodiment includes a method that utilizes a disubstituted furan to produce oleo-methylfuran sulfonic acids via the following exemplary reaction scheme, Scheme 3:



Scheme 3

[49] Scheme 3 illustrates oleo-furan sulfonation method using a disubstituted furan to produce at least two of the three illustrated oleo-methylfuran sulfonic acids with mole ratios a, b, and c, where tuning of reaction parameters 1-5 can used to achieve controlled selectivity for different mole ratios of the sulfonic acid products shown.

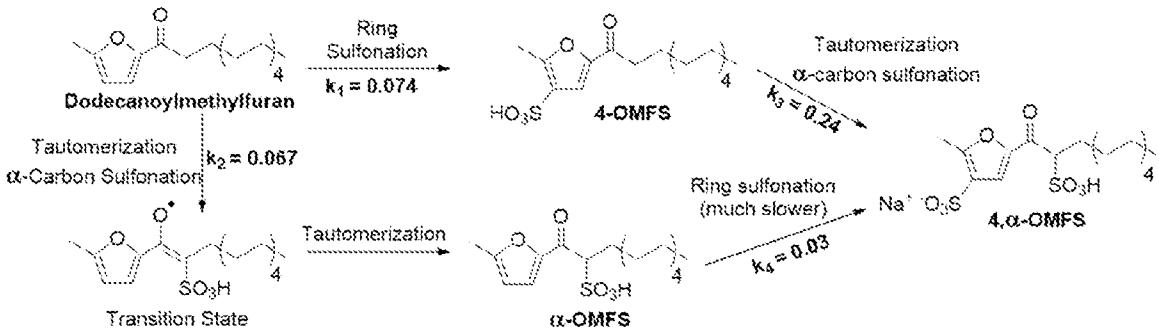
[50] As also noted, an additional embodiment includes a method that includes an oleo-furan sulfonic acid neutralization process to produce oleo-methylfuran sulfonate surfactant salts via the following exemplary reaction scheme, Scheme 4:



Scheme 4

[51] Scheme 4 illustrates an oleo-furan sulfonic acid neutralization process to produce oleo-methylfuran sulfonate surfactant salts with mole ratios a, b, and c, with adjustment of surfactant cation controlled by selection of base used in the neutralization process.

[52] Finally, as also noted, another embodiments includes a method that includes sulfonation of dodecanoylmethylfuran with sulfuric acid sulfonating agent via the following exemplary reaction scheme, Scheme 5:



Scheme 5

[53] Scheme 5 illustrates reaction mapping and rate constants for the sulfonation of dodecanoylmethylfuran with sulfuric acid sulfonating agent (with mole ratios sulfuric acid: dodecanoylmethylfuran in the range from 1:1 to 3.8:1) using acetonitrile solvent in a temperature range between 40°C and 50°C. The mechanism is shown for formation of ring (4-OMFS) and chain (α-OMFS) monosulfonic acids as well as a combined disulfonic acid product (4,α-OMFS) formed from a secondary sulfonation of either the ring or α monosulfonic acids.

[54] Exemplary details relating to the disclosed reaction steps in the various schemes are discussed as follows.

[55] As to sulfonation, sulfonation of oleo-furan compounds was conducted by dissolving or suspending the oleo-furan compound in an organic solvent, or in the absence of solvent (neat), then introducing a sulfonating agent such as oleum or organic sulfur trioxide complexes at the desired temperature in a range from -20°C to 80°C and allowing the contents to combine for a set amount of time in the range of 1 minute (i.e., immediate quenching after addition of sulfonating agent) to 72 hours. In some instances, a secondary sulfonating agent was added to the reaction mixture to further modify the sulfonation reactivity. In some instances, the oleo-furan sulfonating agent mixture were adjusted to a second temperature in the range of -20°C to 80°C for a set period of time to adjust the reactivity and further tune the selectivity of oleo-furan sulfonic acid species produced. The reaction was typically concluded by adding from 10 wt% to 300 wt% water to quench the remaining sulfonating agent, followed by a neutralization step with a base to form oleo-furan surfactants salts. More details on the solvents, methods and reagents used during the sulfonation, quenching, neutralization, or combined quenching-neutralization steps are disclosed in the examples provided herein.

[56] As to acid form neutralization, optional neutralization of the protic monoanionic or diprotic dianionic surfactant can be achieved by slow addition of a base containing the cation

of choice, including but not limited to sodium carbonate, calcium carbonate, sodium hydroxide, or calcium hydroxide, to solution that is either entirely aqueous or that is composed of both water and organic in a mixture, with a ratio is 0-90 v/v% organic solvent by volume, and the organic solvent includes, but is not limited to, nitriles such as acetonitrile, alkanes such as hexanes, or chlorocarbons such as chloroform. This process can result in the surfactant salt with the selected cation in solution, which can then reduced to a solid by heating in a temperature range from 25-80°C while optionally applying vacuum in the pressure range of 1 mTorr-760 Torr. Removal of residual sulfate or carbonate salts in the product mixture, which may be present in varying quantities depending on the sulfonation method and neutralization base salt selected, can be achieved by dissolving the solids in a minimum of water and adding sufficient organic solvent, including but not limited to acetone, to prepare a 1:1 aqueous to organic solvent solution by volume. This solution can be mixed thoroughly, then can stored at a temperature between 0 and 15°C for a period of time from 1-48 hours. The solid salt can then removed by filtration, and the surfactant can be recovered from the filtrate by heating in a temperature range from 25-80°C while optionally applying a vacuum in the pressure range of 1 mTorr-760 Torr to dry the surfactant product. If unsulfonated organics or sulfated byproducts remain in the product mixture, removal can be achieved by recrystallization in organic solvent including but not limited to water, isopropanol, ethanol, methanol, acetonitrile, acetone, or mixtures composed of, but not limited to, the aforementioned solvents.

[57] The methods disclosed herein can be carried out using any of a variety of feedstocks. As examples, feedstocks used in the process can include one or more of, but are not limited to, oleo-furans and substituted oleo-furans including but not limited to decanoylfuran, dodecanoylfuran, tetradecanoylfuran, hexadecanoylfuran, octadecanoylfuran, decanoylmethylfuran, dodecanoylmethylfuran, tetradecanoylmethylfuran, hexadecanoylmethylfuran, octadecanoylmethylfuran, with carbon chain lengths varying from (C_6 to C_{26}) that can be saturated or unsaturated (mono-, di-, or tri-), and solvents.

[58] Solvents used for sulfonation of oleo-furans and the optional neutralization of the oleo-furan sulfonic acids as well as the optional surfactant purification can include, for example, one or more of ketones including acetone and methylethylketone, hydrocarbons including but not limited to pentane, hexane, and heptane, cyclohexane, and cyclopentane, aromatic organics including benzene, toluene, organic nitriles including acetonitrile, propionitrile, and butyronitrile, organic chlorocarbons including dichloromethane, dichloroethane, chloroform, alcohols including but not limited to methanol, ethanol, and

isopropanol, ethereal solvents including but not limited to dimethyl ether, diethyl ether, and tetrahydrofuran, esters including but not limited to methyl acetate and ethyl acetate, water and finally the absence of solvent (neat).

[59] Method embodiments disclosed herein can be carried out to produce various compound embodiments within the scope of the present disclosure. One such exemplary embodiment includes a compound having the formula General Structure 1 or "GS1," shown previously.

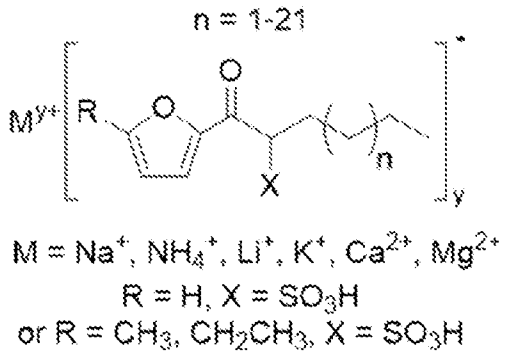
[60] Other compound embodiments within the scope of the present disclosure can be based on the formula of General Structure 1. General Structure 1 and the other disclosed compound embodiments based thereon can provide unique characteristics and performance in comparison to prior oleo-furan surfactants. General Structure 1 and the other disclosed compound embodiments based thereon constitute a new class of oleo-furan surfactant, with a sulfonate moiety positioned either on the alkyl chain adjacent to the ketone functional group (position 4), or on both the furan ring (positions 1-3) and alkyl chain adjacent to the ketone functional group (position 4), representing a dianionic, disulfonate surfactant species. These mono- and dianionic sulfonate surfactants can be charge balanced with a number of cations including, for example, but not limited to, Na^+, Ca^{2+}, Mg^{2+}, Li^+, K^+, and NH_4^+.

[61] For the compound embodiments based on General Structure 1 and disclosed herein, as well as General Structure 1 itself, the alkyl chain length either on the terminal end of the furan moiety including the carbon atom connected to the furan ring containing an acyl functional group can vary from n=1 to n=21 (C_6 to C_{26}, respectively) preferably being in the alkyl chain range of n=1 to n=13 (C_6 to C_{18}, respectively), more preferably being in the alkyl chain range of n=3 to n=13 (C_8 to C_{18}, respectively), and most preferably being in the alkyl chain range of n=5 to n=13 (C_{10} to C_{18}, respectively). In various embodiments, the length of the alkyl chain can be a critical surfactant structural feature and varied alkyl chain length can alter surfactant characteristics, including factors that impact performance in various applications, e.g., laundry detergency. For these reasons, alkyl chain lengths in one range, e.g., C_1-C_5, are generally considered to produce surfactants with significantly different application performance than those in another range, e.g., C_6-C_{26}.

[62] In the depicted composition structure of the embodiment of General Structure 1 above, functional groups designated by numbers 1-4 can include -H, $-CH_3$, $-CH_2CH_3$, a longer alkyl chain, -OH, polyglycoside, polyethoxylate, sulfate and sulfonate. More preferably, these functional group could include -H, $-CH_3$, sulfonate, sulfate, polyglycoside,

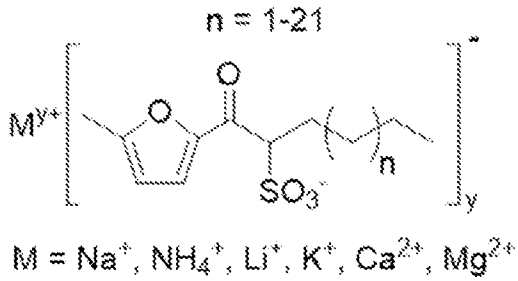
and polyethoxylate. Most preferably, these functional groups could include -H, -CH_3, sulfate and sulfonate.

[63] One embodiment of a surfactant composition structure based on General Structure 1 is depicted as follows as Structure A of General Structure 1:



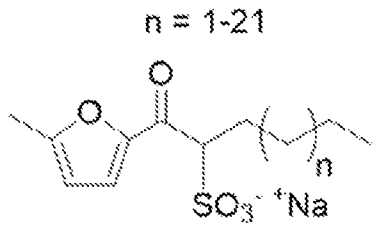
Structure A of General Structure 1

[64] A further embodiment of Structure A can include a surfactant structure depicted as follows as Structure A1 of General Structure 1:



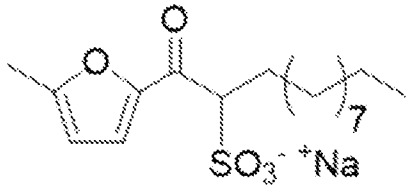
Structure A1 of General Structure 1

[65] A yet further embodiment of Structure A, and also of Structure A1, can include a surfactant structure depicted as follows as Structure A2 of General Structure 1:



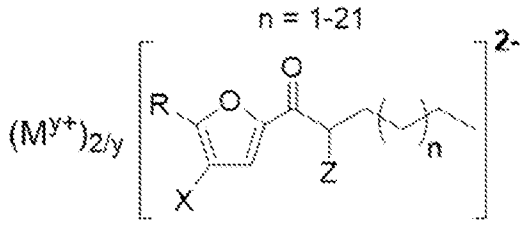
Structure A2 of General Structure 1

[66] A particular embodiment of Structure A2, and thus also of Structure A, can include a surfactant structure depicted as follows as Structure A2-1 of General Structure 1:



Structure A2-1 of General Structure A

[67] Another embodiment of a surfactant composition structure based on General Structure 1 is depicted as follows as Structure B of General Structure 1:



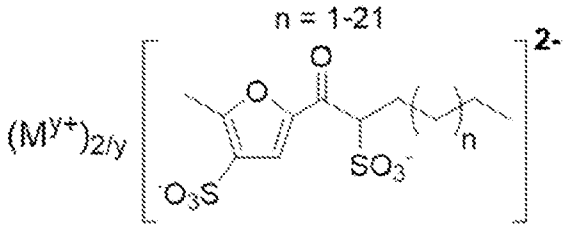
$M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}$

$R = SO_3^-, X = H, Z = SO_3^-$

or $R = CH_3, CH_2CH_3, X = SO_3^-, Z = SO_3^-$

Structure B of General Structure 1

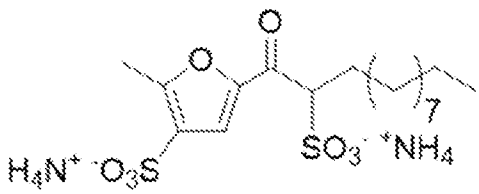
[68] A further embodiment of Structure B can include a surfactant structure depicted as follows as Structure B1 of General Structure 1:



$M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}$

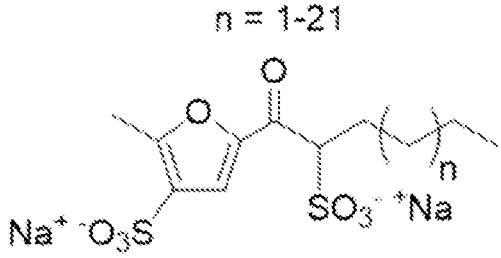
Structure B1 of General Structure 1

[69] A particular embodiment of Structure B1, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B1-1 of General Structure 1:



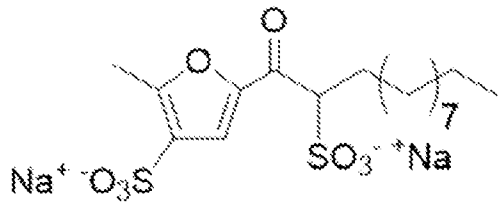
Structure B1-1 of General Structure 1

[70] A further embodiment of Structure B, and also of Structure B1, can include a surfactant structure depicted as follows as Structure B2 of General Structure 1:



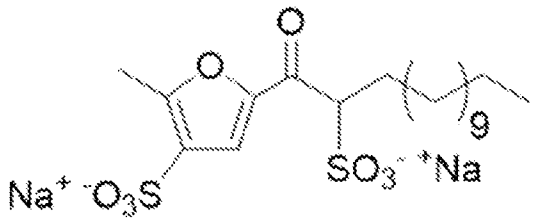
Structure B2 of General Structure 1

[71] A particular embodiment of Structure B2, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B2-1 of General Structure 1:



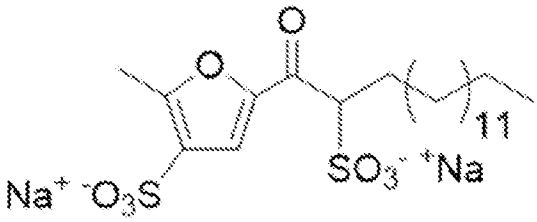
Structure B2-1 of General Structure 1

[72] Another particular embodiment of Structure B2, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B2-2 of General Structure 1:



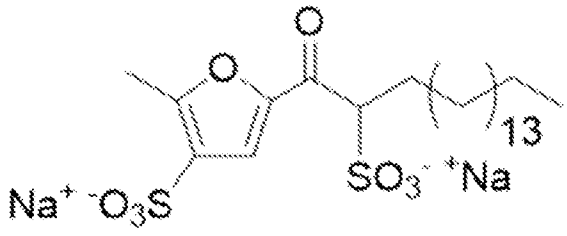
Structure B2-2 of General Structure 1

[73] Yet another particular embodiment of Structure B2, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B2-3 of General Structure 1:



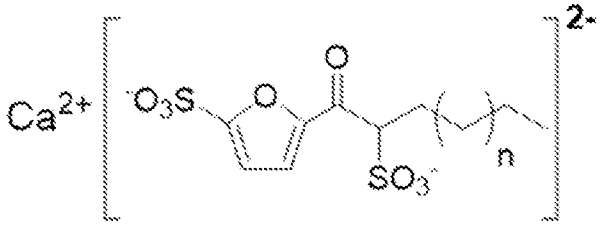
Structure B2-3 of General Structure 1

[74] Yet another particular embodiment of Structure B2, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B2-4 of General Structure 1:



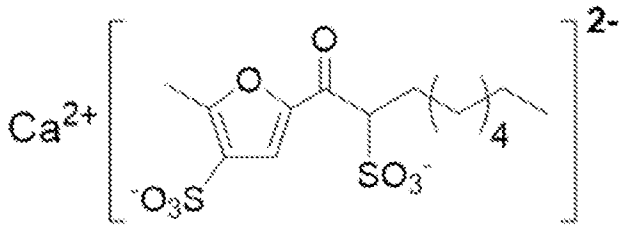
Structure B2-4 of General Structure 1

[75] A further embodiment of Structure B can include a surfactant structure depicted as follows as Structure B3 of General Structure 1:



Structure B3 of General Structure 1

[76] Another embodiment of Structure B3, and thus also of Structure B, can include a surfactant structure depicted as follows as Structure B3-1 of General Structure 1:



Structure B3-1 of General Structure 1

[77] The following describes an example of a general reaction method for oleo-furan sulfonation.

[78] An oleo-furan compound can be dissolved in a solvent including, but not limited to, alkanes such as hexane and heptane, nitriles such as acetonitrile or propionitrile, or chlorocarbons such as dichloromethane and chloroform, at a concentration ranging between 0.001 M to 1 M, or is used in the absence of solvent (neat). The oleo-furan compound or solution is then cooled or heated to a temperature in the range of -20°C to 80°C, more preferably in the range of 0°C to 60°C, and most preferably in the range of 0°C to 40°C, after which a sulfonating agent can be added, including but not limited to sulfur trioxide organic complexes such as SO_3•pyridine, SO_3•dimethylaniline, SO_3•dimethylformamide, SO_3•triethylamine, SO_3•trimethylamine, and SO_3•quinoline, chlorosulfonic acid, sulfuric acid, sodium sulfate, sodium bisulfate, sulfamic acid, or oleum (e.g., fuming sulfuric acid

with an SO_3 active concentration range from 5 wt% to 65 wt%) at a molar ratio loading of sulfonating agent to oleo-furan from 0.5 to 6.4, more preferably at a sulfonating agent to oleo-furan ratio of 0.5 to 3.2, and most preferably at a sulfonating agent to oleo-furan ratio of 0.5 to 2. A second sulfonating agent is optionally added to augment the reactivity of the first sulfonating agent, including but not limited to all sulfonating agents listed above, at a molar ratio loading of sulfonating agent to oleo-furan from 0.01 to 1, more preferably at a sulfonating agent to oleo-furan ratio of 0.01 to 0.5, and most preferably at a sulfonating agent to oleo-furan ratio of 0.01 to 0.1. The reaction is then stirred for a period of time, which is tailored to the desired level of sulfonation reactivity ranging from 1 minute (e.g., the reaction is quenched immediately after sulfonating agent addition) to 72 hours, more preferably 1 minute to 24 hours, and most preferably 1 minute to 1 hour. After this time, the reaction can be quenched with a mass of water in the range of 10 wt% of the reaction solution's mass to 300 wt%, more preferably 50 wt% to 150 wt%, and most preferably 75 wt% to 150 wt%. After quenching but prior to neutralization, an optional liquid-liquid extraction step can be performed by adding a solvent including but not limited to alkanes such as hexanes or heptane to remove unsulfonated oleo-furan materials from the aqueous sulfonated products. The quenched sulfonic acid solutions can then optionally be treated with a basic aqueous solution including, but not limited to, sodium hydroxide, calcium hydroxide, magnesium hydroxide, potassium hydroxide, or lithium hydroxide in the concentration range of 1-50 w/v % with mass of base solution added in the range of 10 wt% to 300 wt% of the sulfonation reaction's mass, targeting a final surfactant solution pH in the range of 4-10. As an alternative to quenching the reaction with deionized water and separately neutralizing the sulfonic acids with a base solution after, the reaction can optionally be quenched and neutralized simultaneously by adding a basic aqueous solution including, but not limited to, sodium hydroxide, calcium hydroxide, magnesium hydroxide, potassium hydroxide, or lithium hydroxide in the concentration range of 1-50 w/v % with mass of solution added in the range of 10 wt% to 300 wt% of the sulfonation reaction's mass, targeting a final surfactant solution pH in the range of 4-10.

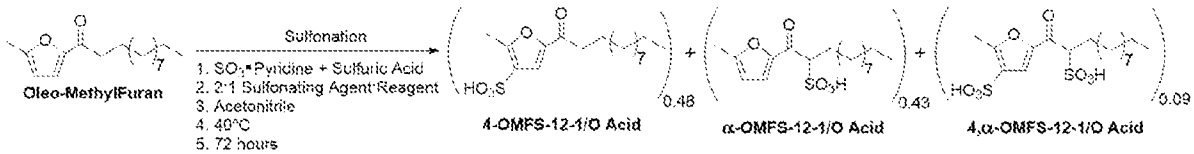
[79] Described below are exemplary, non-limiting methods that follow the general experimental methods listed above and fit the general sulfonation reaction scheme illustrated above as Scheme 1. Methods and analysis provided in the following method descriptions include the subsequent neutralization step (illustrated in Scheme 2 above); however, these methods do not require neutralization to achieve the designated selectivity for the produced

sulfonic acids, and in some embodiments the neutralization step may be omitted for production of the oleo-furan sulfonic acid blends.

Example 1

[80] Example 1 describes embodiments of an oleo-methylfuran sulfonate (OMFS) surfactant blends having one or more synergistic properties and exemplary methods of synthesizing such surfactant blend embodiments.

[81] A 0.37 M solution of dodecanoylmethylfuran in acetonitrile was prepared and heated to 40°C, after which time SO_3•pyridine was added in a mole ratio of 2:1 sulfonating agent to dodecanoylmethylfuran. Sulfuric acid is then added in a mole ratio of 0.05:1 sulfonating agent to dodecanoylmethylfuran, and the reaction is allowed to stir for 72 hours, after which time the reaction was quenched by adding a mass of deionized water equal to 100% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 48:43:9. The SO_3 actives determined by Hyamine active titration (performed according to ASTM D4251) was 87%, and the total surfactant yield was 29%. The reaction scheme representing this method, including oleo-furan reagent(s) used and product distribution, can be seen in Scheme 6. The sodium-OMFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with sodium hydroxide solution to a pH of 7.5 can be seen in Figure 1, and the ^{1}H NMR spectrum of the sodium surfactant blend can be referenced in Figure 2. The calcium-OMFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with calcium hydroxide solution to a pH of 7 can be seen in Figure 3. The magnesium-OMFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with magnesium hydroxide solution to a pH of 7.5 can be seen in Figure 4. The properties of the sodium, calcium and magnesium surfactant blends are reported in Table 1.



Scheme 6

[82] Scheme 6 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for Example 1.

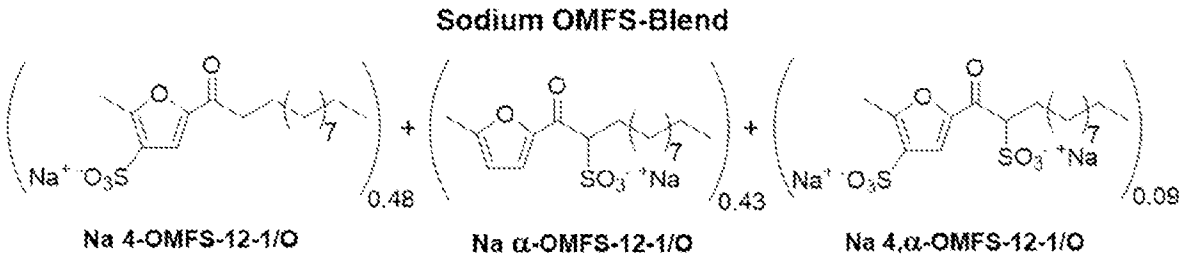


Figure 1

[83] Figure 1 illustrates oleo-furan surfactants formed from neutralization of sulfonic acids produced from methods detailed above for Example 1 1 using a sodium hydroxide solution to achieve a final pH of 7.5.

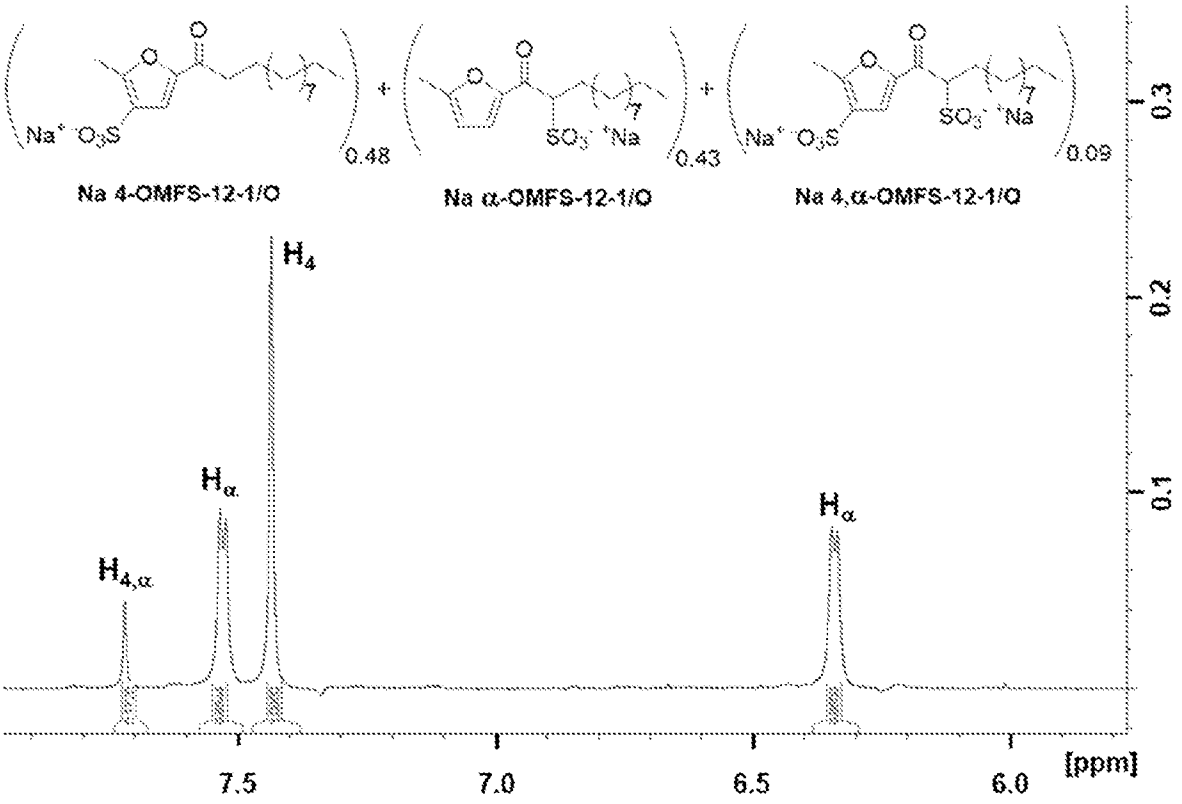


Figure 2

[84] Figure 2 illustrates ^{1}H NMR spectra of sodium OMFS-Blend showing the aromatic proton signal region and the specific proton signals corresponding to individual sulfonate species in the blend.

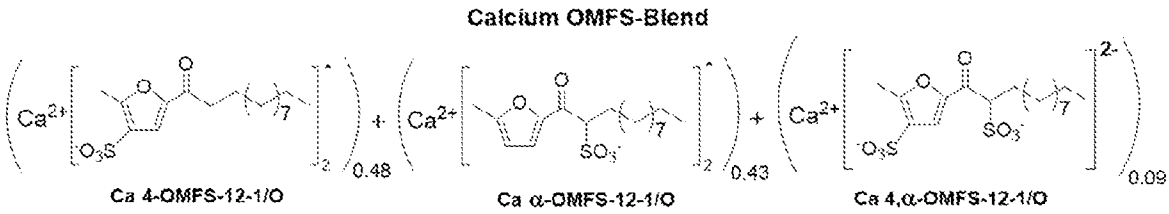


Figure 3

[85] Figure 3 illustrates oleo-furan surfactants formed from neutralization of sulfonic acids produced from methods detailed above for Example 1 using a calcium hydroxide solution to achieve a final pH of 7.

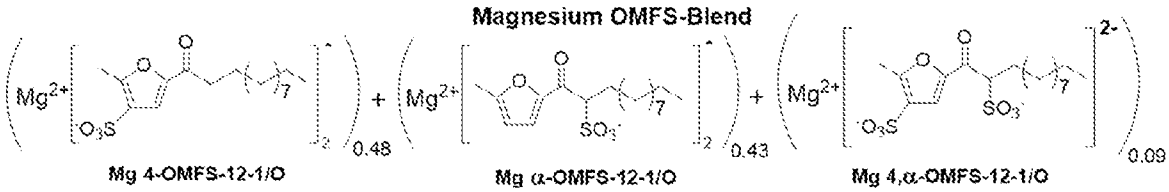


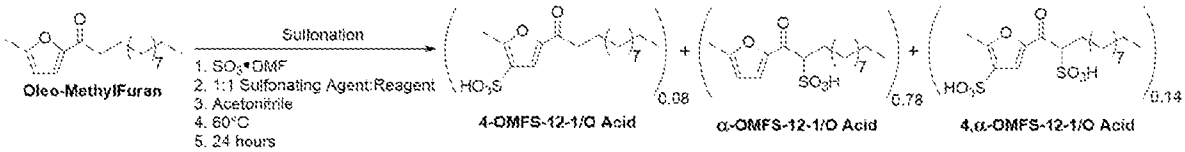
Figure 4

[86] Figure 4 illustrates oleo-furan surfactants formed from neutralization of sulfonic acids produced from methods detailed above for Example 1 using a magnesium hydroxide solution to achieve a final pH of 7.5.

Example 2

[87] Example 2 describes method embodiments for primary selectivity to α-OMFS surfactant (C_{12} alkyl chain) embodiments.

[88] A 0.15 M solution of dodecanoylmethylfuran in acetonitrile was prepared and heated to 60°C, after which time SO3●dimethylformamide was added in a mole ratio of 1:1 sulfonating agent to dodecanoylfuran. The reaction was allowed to stir for 24 hours, after which time the reaction was quenched by adding a mass of deionized water equal to 100% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by 1H NMR was 8:78:14. The total reaction yield was 41%. The reaction scheme representing this method, including oleo-furan reagent(s) used and product distribution, can be seen in Scheme 7.



Scheme 7

[89] Scheme 7 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for Example 2.

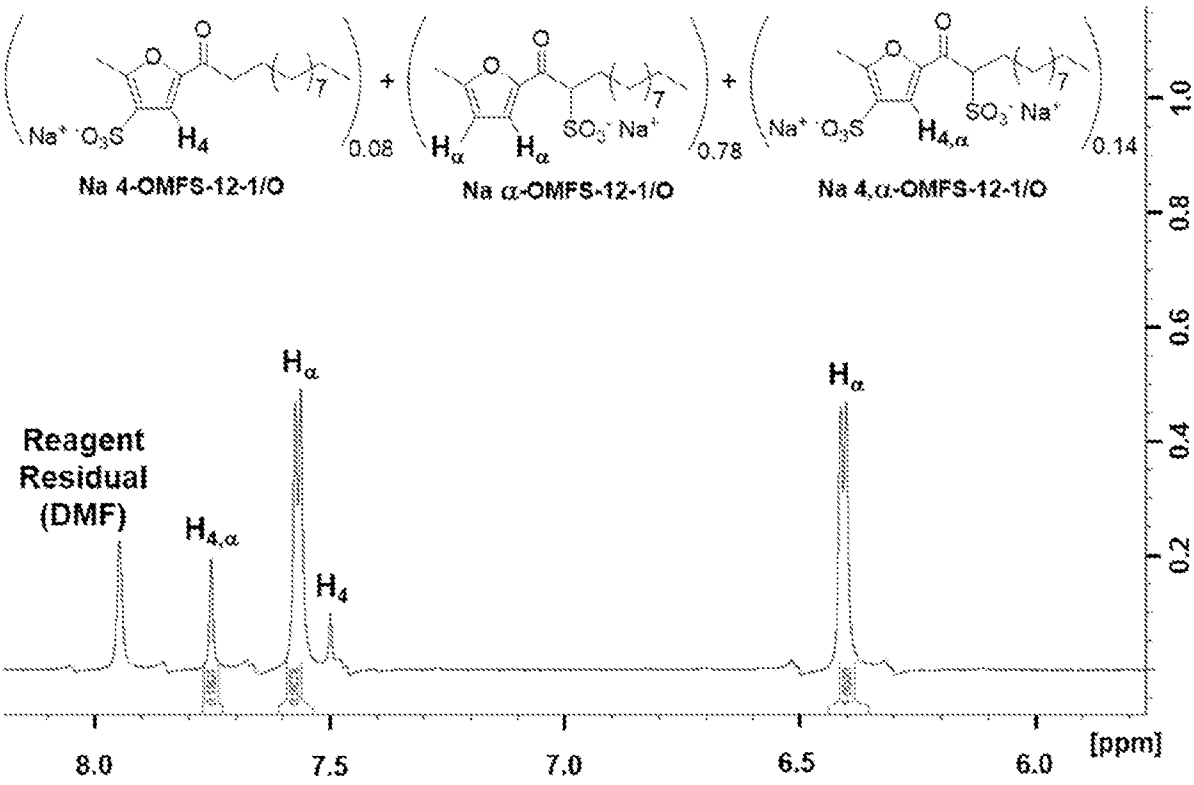


Figure 5

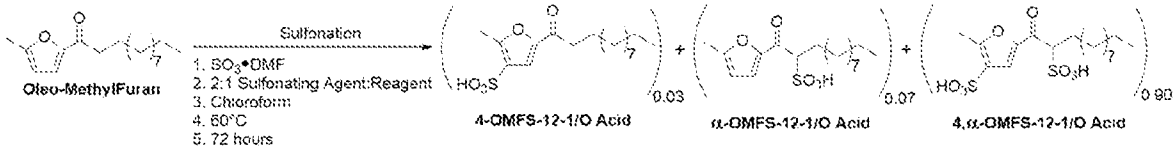
[90] Figure 5 illustrates ^{1}H NMR spectra of sodium surfactant blend produced by the technique described above for Example 2 after neutralization with sodium hydroxide, showing the aromatic proton signal region and the specific proton signals corresponding to individual sulfonate species in the blend.

Example 3

[91] Example 3 describes method embodiments for primary selectivity to 4,α-OMFS surfactant (C_{12} alkyl chain) embodiments.

[92] A 0.76 M solution of dodecanoylmethylfuran in acetonitrile was prepared and heated to 60°C, after which time SO_3•dimethylformamide was added in a mole ratio of 2:1 sulfonating agent to dodecanoylfuran. The reaction was allowed to stir for 72 hours, after which time the reaction was quenched by adding a mass of deionized water equal to 100% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 3:7:90. The total reaction yield was 70%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction

conditions used as well as product distribution, can be seen in Scheme 8. The sodium-OMFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with sodium hydroxide solution to a pH of 7.8 as well as the ^{1}H NMR spectrum of the sodium surfactant blend can be referenced in Figure 6.



Scheme 8

[93] Scheme 8 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 3.

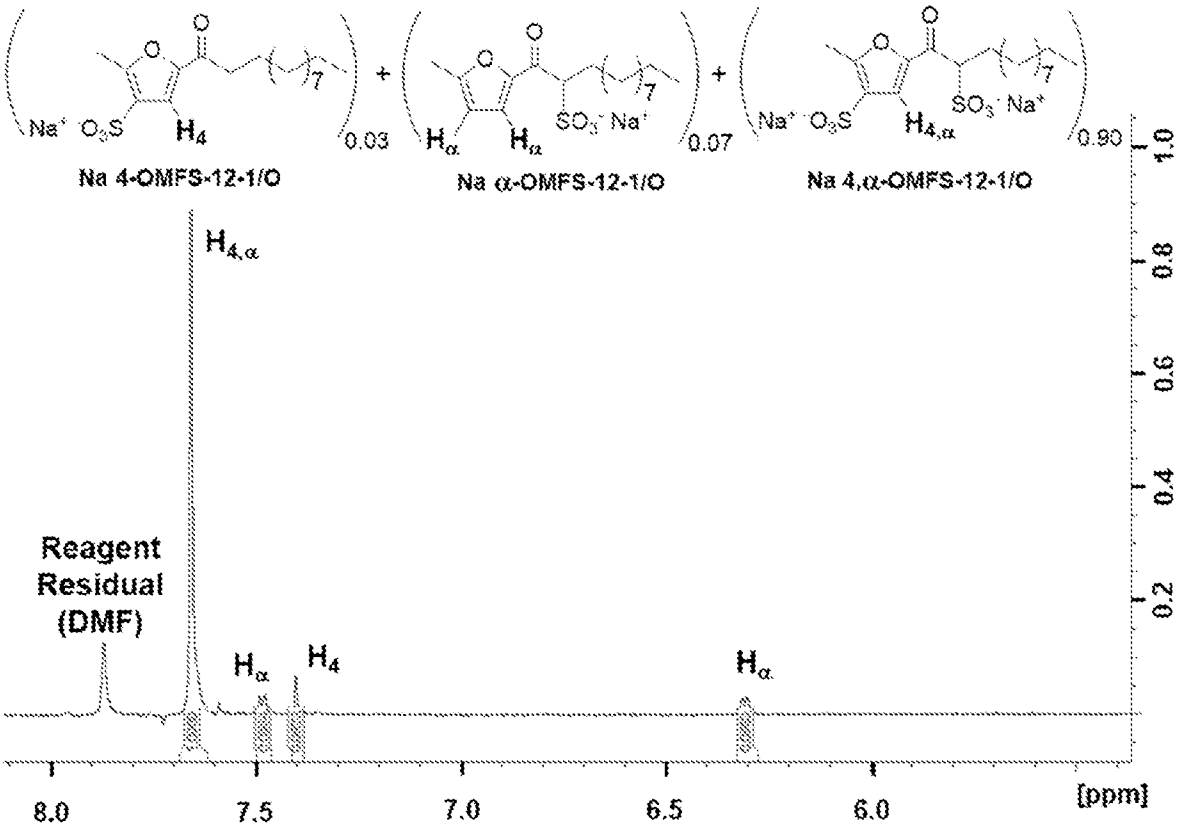


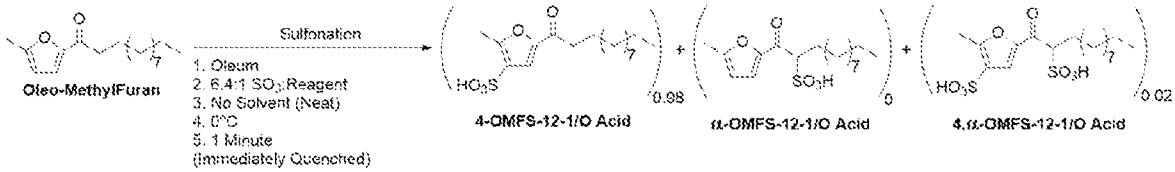
Figure 6

[94] Figure 6 illustrates ^{1}H NMR spectra of sodium surfactant blend produced per the technique described here for Example 3 after neutralization with sodium hydroxide to a pH of 7.8, showing the aromatic proton signal region and the specific proton signals corresponding to individual sulfonate species in the blend.

Example 4

[95] Example 4 describes method embodiments for primary selectivity to 4-OMFS surfactant (C_{12} alkyl chain) embodiments.

[96] Oleum (10 mL, 20 wt% SO_3) in the absence of solvent (neat) was cooled to 0°C and 2 g dodecanoylfuran was added with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 6.4:1. Immediately after oleum addition, the reaction was quenched by adding a mass of deionized water equal to 100% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 98:0:2. The total reaction yield was 29%. The reaction scheme representing this method embodiment, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 9 below.



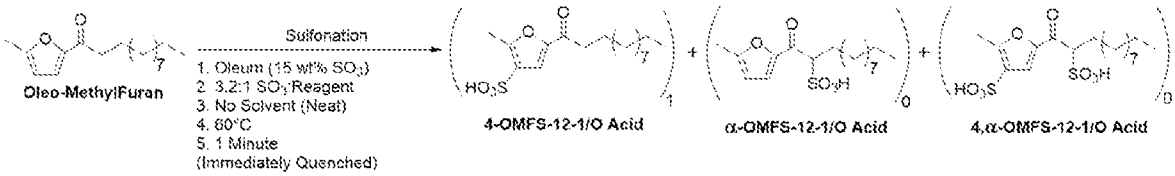
Scheme 9

[97] Scheme 9 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 4.

Example 5

[98] Example 5 describes alternate method embodiments, relative to Example 4, for primary selectivity to 4-OMFS surfactant (C_{12} alkyl chain) embodiments.

[99] 3 g of dodecanoylmethylfuran was heated to 60°C in a jacketed flask in the absence of solvent (neat), to which oleum (10 mL, 15 wt% SO_3) was added dropwise with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 3.2:1. Immediately after oleum addition, the reaction was quenched by adding a mass of deionized water equal to 100% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 100:0:0. The total reaction yield was 13%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 10. The sodium-OMFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with sodium hydroxide solution to a pH of 8 can be seen in Figure 7.



Scheme 10

[100] Scheme 10 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 5.

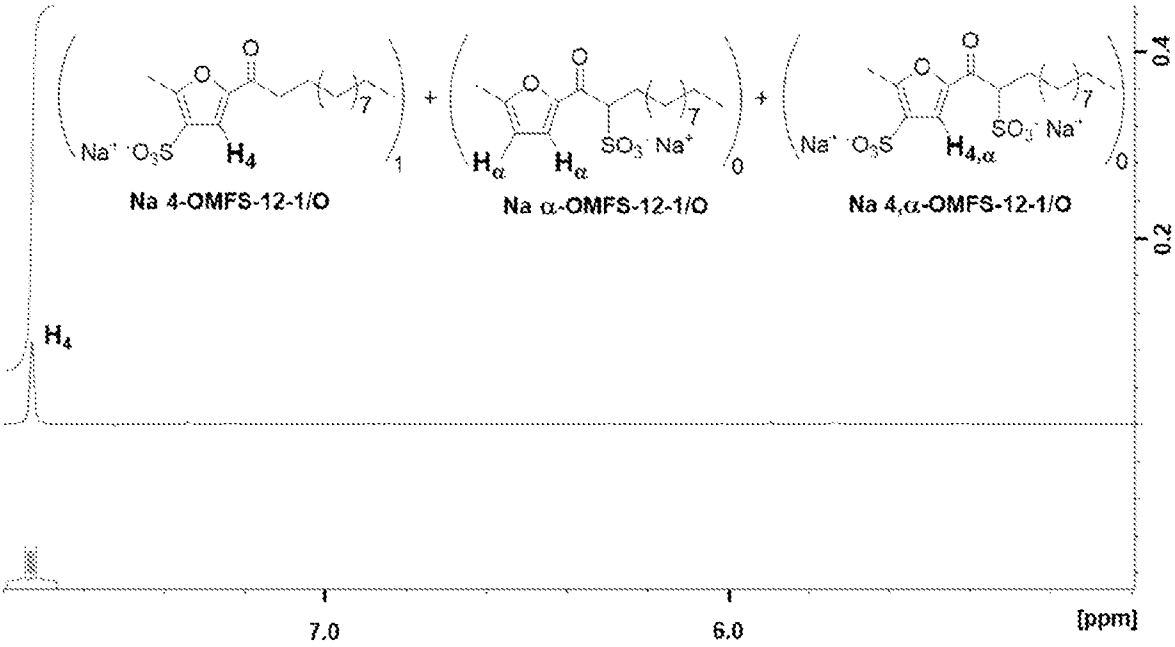


Figure 7

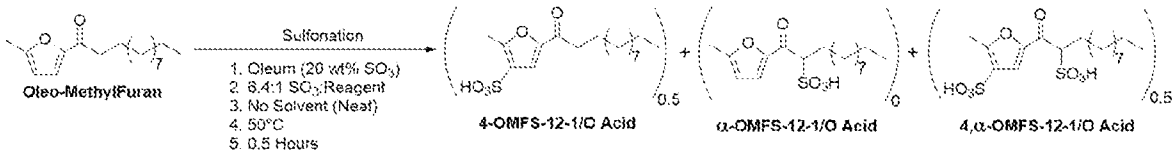
[101] Figure 7 illustrates ^{1}H NMR spectra of sodium surfactant produced by an embodiment per Example 5 after neutralization with sodium hydroxide to a pH of 8, showing the aromatic proton signal region and the specific proton signal corresponding to the Na 4-OMFS-12-1/O surfactant species.

Example 6

[102] Example 6 describes method embodiments for equimolar selectivity to 4-OMFS and 4,α-OMFS surfactant (C_{12} alkyl chain) embodiments.

[103] Oleum (20 mL, 20 wt% SO_3) in the absence of solvent (neat) was cooled to 0°C and 4 g dodecanoylfuran was added with stirring to provide a SO3 to dodecanoylfuran molar ratio of 6.4:1. Immediately after oleum addition, the reaction was heated to 50°C and allowed to stir for 0.5 hours. The reaction was then quenched by addition of 35 reaction wt% deionized water. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as

determined by ^{1}H NMR was 50:0:50. The total reaction yield was 2%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 11.



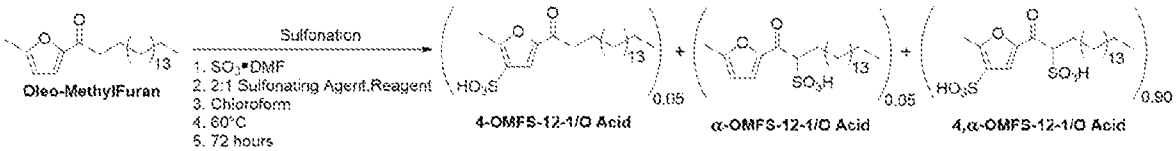
Scheme 11

[104] Scheme 11 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 6.

Example 7

[105] Example 7 describes method embodiments for primary selectivity to 4,α-OMFS surfactant (C_{18} alkyl chain) embodiments.

[106] A 0.16 M solution of octadecanoylmethylfuran in chloroform (4 g in 100 mL) was prepared and heated to 60°C, to which SO_3•dimethylformamide was added in a mole ratio of 2:1 sulfonating agent to dodecanoylfuran. The reaction was allowed to stir for 72 hours, after which time the reaction was quenched with 100 reaction wt% deionized water. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 5:5:90. The total reaction yield was 70%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 12.



Scheme 12

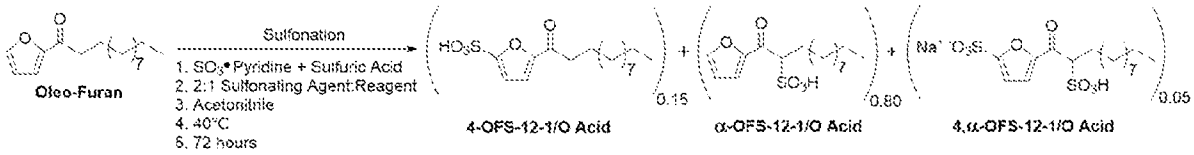
[107] Scheme 12 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 7.

Example 8

[108] Example 8 describes an embodiment relating to preparation of an EFS surfactant blend.

[109] A 0.37 M solution of dodecanoylfuran in acetonitrile was prepared and heated to 40°C, after which time SO3●pyridine was added in a mole ratio of 2:1 sulfonating agent to

dodecanoylmethylfuran. Sulfuric acid is then added in a mole ratio of 0.05:1 sulfonating agent to dodecanoylmethylfuran, and the reaction is allowed to stir for 72 hours, after which time the reaction was quenched with 100 reaction wt% deionized water. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 15:80:5. The total surfactant yield was 26%. The reaction scheme representing this method, including oleo-furan reagent(s) used and product distribution, can be seen in Scheme 13. The sodium-OFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with sodium hydroxide solution to a pH of 8 can be seen in Figure 8, and the properties of this blend are reported in Table 1.



Scheme 13

[110] Scheme 13 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 8.

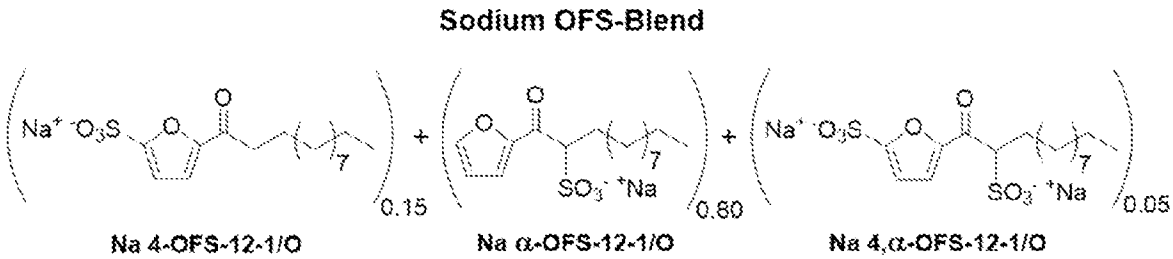


Figure 8

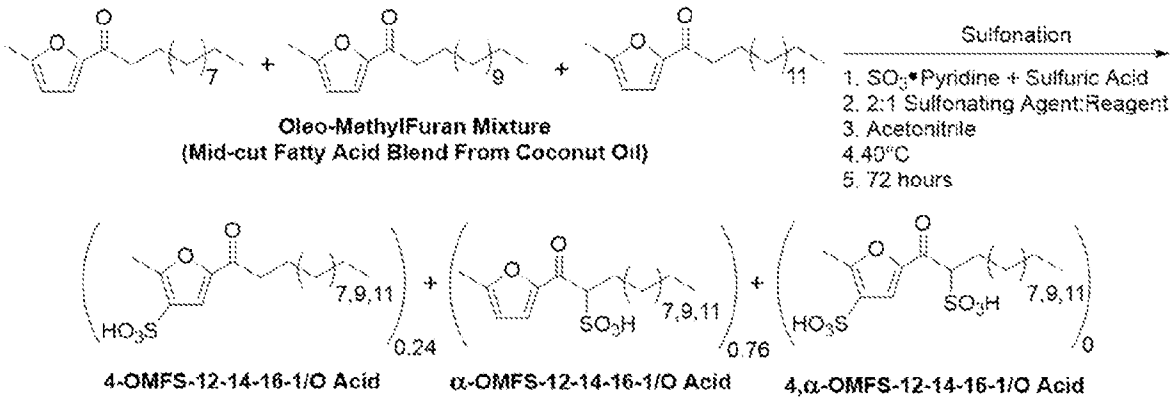
[111] Figure 8 illustrates oleo-furan surfactants formed from neutralization of sulfonic acids produced from methods detailed in Example 8 using a sodium hydroxide solution to achieve a final pH of 8.

Example 9

[112] Example 9 describes an embodiment relating to sulfonation of an oleo-furan mixture derived from a coconut fatty acid blend.

[113] A solution containing 0.091 M dodecanoylmethylfuran, 0.04 M tetradecanoylmethylfuran, and 0.018 M hexadecanoylmethylfuran representative of a mid-cut blend of fatty acids from fractionated coconut oil dissolved in acetonitrile was prepared and heated to 40°C, after which time SO_3•pyridine was added in a mole ratio of 2:1 sulfonating agent to alkanoylfuran (total molar loading of dodecanoylmethylfuran,

tetradecanoylmethylfuran, and hexadecanoylmethylfuran). Sulfuric acid is then added in a mole ratio of 0.05:1 sulfonating agent to dodecanoylmethylfuran, and the reaction was allowed to stir for 72 hours, then the reaction was quenched by adding a mass of deionized water equal to 100%. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 24:76:0. The total reaction yield was 42%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 14.



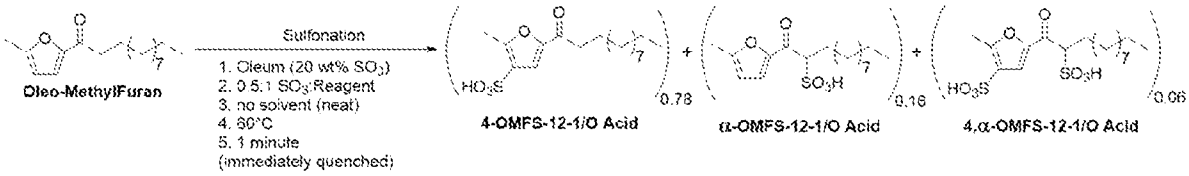
Scheme 14

[114] Scheme 14 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 9.

Example 10

[115] Example 10 describes an embodiment relating to sulfonation of oleo-furans using a sub-stoichiometric loading of sulfonating agent (C_{12} alkyl chain).

[116] 4 g of dodecanoylmethylfuran was heated to 60°C in a jacketed flask in the absence of solvent (neat), to which oleum (1.6 mL, 20 wt% SO3) was added dropwise with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 0.5:1. Immediately after oleum addition, after which time the reaction was quenched by adding a mass of deionized water equal to 75% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 78:16:6. The total reaction yield was 9%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 15.



Scheme 15

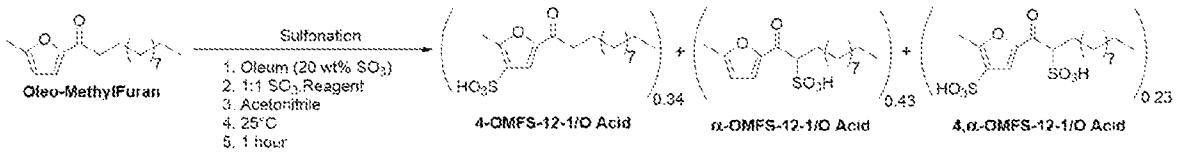
[117] Scheme 15 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 10.

[118] Examples 11-13, described below, disclose the impact of solvent selection on the sulfonation of oleo-furans with oleum sulfonating agent (20 wt% free SO_3); all other reaction conditions were held constant. As can be seen below, incorporating a solvent (compared to neat reactions) and solvent selection resulted in notable differences in both surfactant selectivity and yield, suggesting solvent effects play an important role in moderating solubility, reactivity, heat transfer and proton conductivity during oleo-furan sulfonation.

Example 11

[119] Example 11 describes an embodiment relating to oleum sulfonation with acetonitrile solvent.

[120] A 0.19 M solution of dodecanoylmethylfuran in acetonitrile solvent was heated to 25°C, to which oleum (1.6 mL, 20 wt% SO_3) was added dropwise with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 1:1. The reaction was allowed to stir for 1 hour, after which time the reaction was quenched by adding a mass of deionized water equal to 60% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 34:43:23. The total reaction yield was 68%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 16. The sodium-OFS surfactant blend yielded by neutralization of the sulfonation acids produced by this method with sodium hydroxide solution to a pH of 7.6 can be seen in Figure 9, and the properties of this blend are reported in Table 1.



Scheme 16

[121] Scheme 16 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 11.

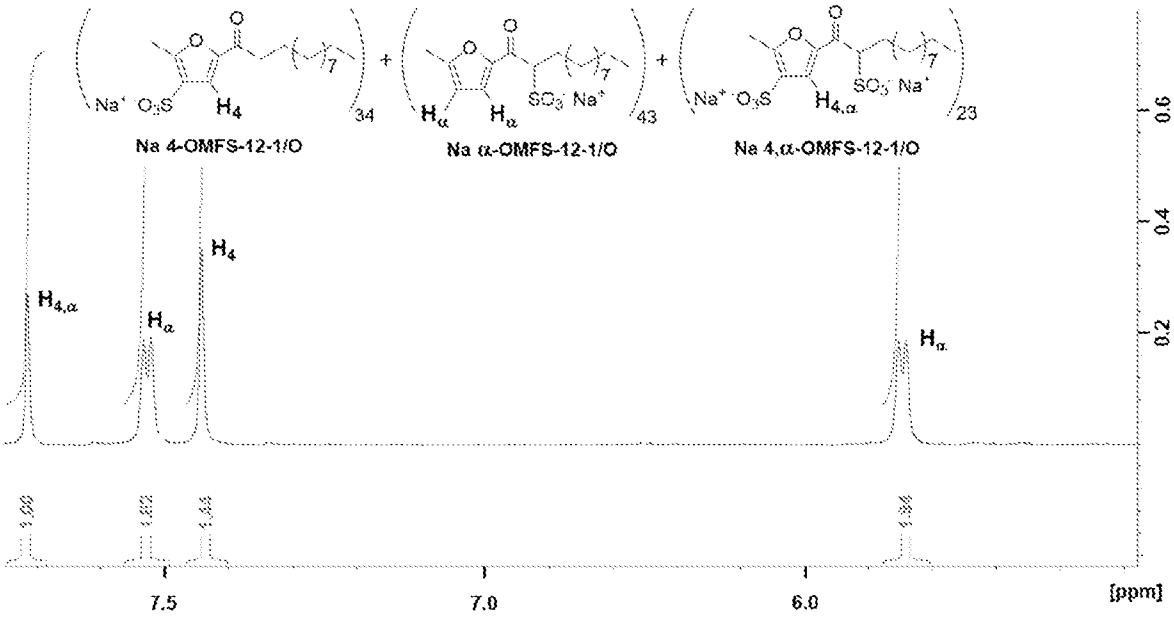


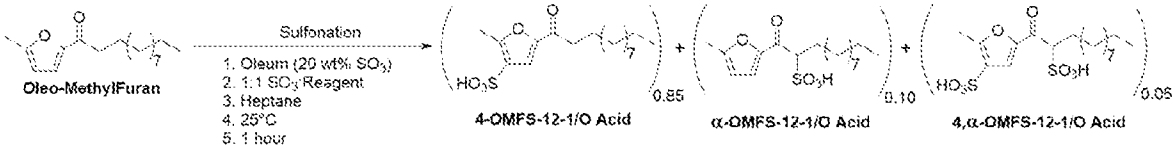
Figure 9

[122] Figure 9 illustrates ^{1}H NMR spectra of sodium surfactant produced per Example 11 after neutralization with sodium hydroxide to a pH of 7.6, showing the aromatic proton signal region and the specific proton signals corresponding to individual sulfonate species in the blend.

Example 12

[123] Example 12 describes an embodiment relating to oleum sulfonation with heptane solvent.

[124] A 0.19 M solution of dodecanoylmethylfuran in heptane solvent was heated to 25°C, to which oleum (1.6 mL, 20 wt% SO_3) was added dropwise with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 1:1. The reaction was allowed to stir for 1 hour, after which time the reaction was quenched by adding a mass of deionized water equal to 60% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 85:10:5. The total reaction yield was 21%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 17.



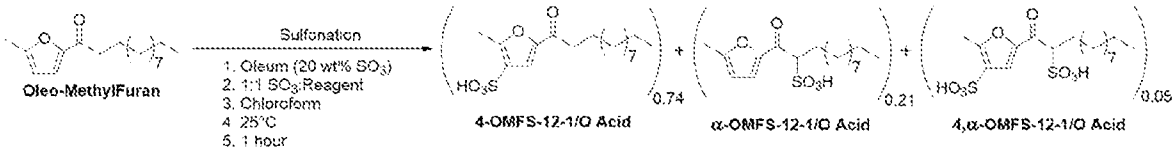
Scheme 17

[125] Scheme 17 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 12.

Example 13

[126] Example 13 describes an embodiment relating to oleum sulfonation with chloroform solvent.

[127] A 0.19 M solution of dodecanoylmethylfuran in chloroform solvent was heated to 25°C, to which oleum (1.6 mL, 20 wt% SO_3) was added dropwise with stirring to provide a SO_3 to dodecanoylmethylfuran molar ratio of 1:1. The reaction was allowed to stir for 1 hour, after which time the reaction was quenched by adding a mass of deionized water equal to 45% of the reaction mass. The percent molar distribution of 4-OMFS, α-OMFS, and 4,α-OMFS products as determined by ^{1}H NMR was 74:21:5. The total reaction yield was 14%. The reaction scheme representing this method, including oleo-furan reagent(s) and reaction conditions used as well as product distribution, can be seen in Scheme 18.



Scheme 18

[128] Scheme 18 illustrates reaction conditions and oleo-furan sulfonic acid product distribution for an embodiment per Example 13.

Example Performance Quantifications

[129] Certain surfactant properties and performance metrics of synthesized surfactants structures according to General Structure 1 (GS1), including several exemplary surfactant blends prepared according to the methods disclosed previously herein, were measured. These results are shown in Table 1 below, and include the time required for the surfactant solution to wet cotton fabric, the amount of foam the surfactant generates when agitated (either poured or exposed to high shear), the surfactant's solubility which can impact the potential loading in product formulations, the temperature below which the surfactant forms a solid precipitate (e.g., Krafft Point), and for some surfactants the critical micelle concentration and surface tension. These provided results demonstrate notable differences in performance as a function of the number and position(s) of sulfonate functional groups added to the oleo-furan compound during the sulfonation process. For example, the α-OMFS-12-1/O surfactant with

a sulfonate on the surfactant's alkyl chain provides faster wetting kinetics, as compared to the ring sulfonate 4-OMFS-12-1/O which has slower fabric wetting kinetics yet generates more foam in high shear conditions, or the disulfonate surfactant sulfonated on both the ring and alkyl chain (4,α-OMFS-12-1/O) which has slower fabric wetting and generates less foam than either of the aforementioned monosulfonates surfactants, yet has a higher solubility that can be helpful in building product formulations. Accordingly, these differing performance metrics can be leveraged by selecting the particular disclosed surfactant structure corresponding to the performance metrics useful in a specific application of the surfactant structure.

[130] One particularly notable finding during property testing of surfactant embodiments disclosed herein was discovery of a synergistic effect for combinations of the 3 sulfonation types: ring sulfonation, alkyl chain sulfonation, and combined ring & chain disulfonation. Referencing Table 1 produced below, the surfactant blend prepared according to Example 1 (Scheme 6), for example, after neutralization of the formed sulfonic acids with sodium hydroxide (Figure 1), with a molar ratio of 0.48:0.43:0.09 for the 4-:α-:4,α-OMFS-12-1/O surfactants, has properties and performance metrics that exceed those of its individual components. The fabric wetting time recorded for this blend was 8 seconds, a faster wetting time than the fastest of the three surfactant components (α-OMFS-12-1/O, 18 seconds). Similarly, this surfactant blend was observed to yield higher pour foam (150 mm) than any component surfactant (highest individual 140 mm for α-OMFS-12-1/O), which is particularly notable given that nearly 10 mole % of this blend's composition is the disulfonate surfactant (4,α-OMFS-12-1/O) which generates significantly less foam. These results indicate the properties and performance of oleo-furan sulfonate surfactant blends are not additive, but synergistic and unique to the composition of the blend.

[131] The impact of cation selection on the properties and performance of surfactant blends can be observed by comparison of properties for the sodium-, calcium-, and magnesium-neutralized sulfonic acids prepared according to Example 1. The sodium and calcium surfactant blends have similar fabric wetting kinetics, cold water solubility (Krafft point < 0°C) and foam generation from pouring; however, the calcium surfactant blend has a significantly lower critical micelle concentration, allowing for micelle formation at less than a third of the surfactant loading of the sodium surfactant (250 ppm for calcium vs. 800 ppm for sodium). The sodium surfactant blend was also observed to generate more foam with high shear agitation compared to the sodium surfactant. The magnesium surfactant blend was distinct from both its sodium and calcium counterparts in numerous properties, including a lower solubility (Krafft point of 25°C), slower wetting kinetics, and lower foam generation

with high shear agitation. The magnesium surfactant blend generated more foam from pour testing than either the sodium or calcium blends; this pour foam generation exceeded every other individual surfactant and surfactant blend tested.

[132] The sodium surfactant blends formed by sulfonation and subsequent neutralization of dodecanoylfuran (Example 8) contained a different ratio of the sulfonate product compositions (4-OFS, α-OFS, and 4,α-OFS) compared to the surfactant blends prepared from dodecanoylmethylfuran (Figure 8); however, multiple properties were similar between the sodium OMFS-blend and the sodium OFS-blend surfactants. Cold water solubility and foam generation were similar for the sodium surfactant blends, while critical micelle concentration and fabric wetting kinetics both differed significantly. These differences may be due to either the difference in chemical compositions from an oleo-furan vs. an oleo-methylfuran feedstock, or the difference in ratio of the formed sulfonic acids that are neutralized to make the surfactant blend, or possibly a combination of both.

[133] Preparation of oleo-furan surfactants with higher carbon content, such as using oleo-furan feedstocks prepared from longer alkyl chain fatty acids including tetradecanoylmethylfuran, hexadecanoylmethylfuran, octadecanoylmethylfuran, or mixtures thereof, have generally been found to have a higher carbon content than is beneficial for surfactant performance due to a poor hydrophilic-lipophilic balance (HLB). Compared to the lauric acid-based oleo-furans (e.g., dodecanoylmethylfuran), the oleo-furan feedstocks sourced from longer alkyl chain fatty acids are excessively lipophilic, and as a result tend to exhibit lower foam generation upon agitation as well as lower cold-water solubility (higher Krafft point). The methods outlined above that enable control over the number of sulfonate groups per surfactant molecule have allowed for the design of oleo-furan sulfonate surfactant molecules with higher carbon content (alkyl chain lengths of C_{14}, C_{16}, and C_{18} corresponding to Exemplary Structures 3, 4 and 5, respectively) that have additional sulfonate groups added to balance the HLB and retain preferred surfactant characteristics. For example, the disulfonate surfactants of Structures B2-2, B2-3, and B2-4, which contain a higher carbon content, still exhibit the high pour foam generation that is useful for surfactants in personal care applications, as well as cold-water solubility (Krafft points < 0°C) that is desired for sustainable detergency applications. These disulfonate surfactants by many metrics perform similarly to the monoanionic surfactants with a lower carbon content (e.g., 4-OMFS-12-1/0), which allows for use of a wider range of fatty acid feedstocks with higher carbon content in the surfactant manufacturing process than is generally acceptable for use in anionic surfactants (e.g., sulfated fatty alcohols).

Surfactant or Surfactant Blend	CMC[1] (ppm)	Surface Tension[2] (mN/m)	Pour Foam Height[3] (mm)	High Shear Foam Height[4] (mm)	Wetting Time[5] (sec)	Solubility[6] (g/mL)	Krafft Point (°C)
Na^+ 4-OMFS-12-1/0 (n=12)*	1480	42	134/132	71/69	48	0.8	< 0
Na^+ α-OMFS-12-1/0 (n=12)* Structure A2-1	-	-	140/135	65/65	18	0.8	< 0
Na^+ 4,α-OMFS-12-1/0 (n=12)* Structure B2-1	-	-	75/35	25/15	>300	0.9	< 0
Na^+ 4,α-OMFS-14-1/0 (n=14)* Structure B2-2	-	-	155/145	53/50	>300	0.6	< 0
Na^+ 4,α-OMFS-16-1/0 (n=16)* Structure B2-3	-	-	160/150	40/40	120	0.8	< 0
Na^+ 4,α-OMFS-18-1/0 (n=18)* Structure B2-4	-	-	130/125	40/40	141	-	< 0
NH_4^+ 4,α-OMFS-12-1/0 (n=12)* Structure B1-1	3545	39	60/40	37/31	>300	0.5	< 0
Ca^{2+} 4,α-OFS-12-1/0 (n=12)* Structure B3-1	-	-	70/60	51/48	>300	-	< 0
Na^+ OMFS-Blend (n=12)* Method Example 1 + NaOH	800	32	150/145	71/70	8	0.9	< 0
Ca^{2+} OMFS-Blend (n=12)* Method Example 1 + $Ca(OH)_2$	250	34	150/140	50/50	7	0.4	< 0
Mg^{2+} OMFS-Blend (n=12)* Method Example 1 + $Mg(OH)_2$	-	38	185/175	43/41	22	< 0.1	25
Na^+ OFS-Blend (n=12)* Method Example 8 + NaOH	1735	44	134/118	68/68	34	-	< 0

[1]Critical micelle concentration
[2]Surface tension at critical micelle concentration
[3]Height of foam immediately after foam formation and after 5 minutes (20°C), performed according to ASTM D1173
[4]Height of foam immediately after foam formation and after 5 minutes (20°C), performed according to ASTM D3519
[5]Wetting of cotton skein at 30°C (TestFabrics) according to ASTM D2281
[6]Solubility in deionized water at 20°C
*Here n is defined as the total number of carbon atoms in the alkyl chain of the oleo-furan surfactant

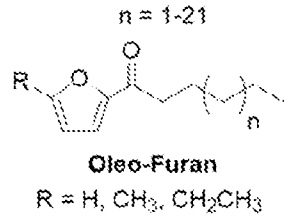
Table 1

[134] Various examples have been described with reference to certain disclosed embodiments. The embodiments are presented for purposes of illustration and not limitation. One skilled in the art will appreciate that various changes, adaptations, and modifications can be made without departing from the scope of the invention.

What is claimed is:

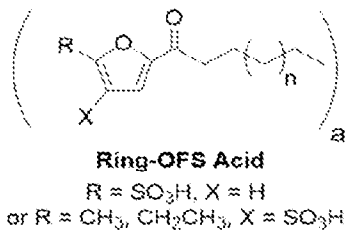
1. A method comprising:

providing an oleo-furan compound according to the formula (1):

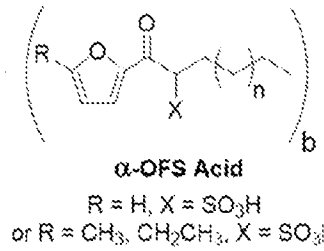


(1); and

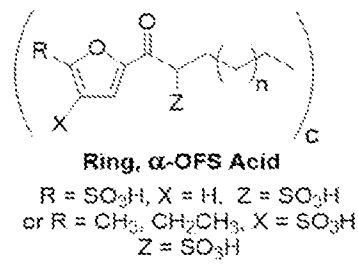
sulfonating the provided oleo-furan compound to produce at least two of a first oleo-furan sulfonic acid according to formula (2), a second oleo-furan sulfonic acid according to formula (3), and a third oleo-furan sulfonic acid according to formula (4):



(2),



(3),



(4),

wherein n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and wherein a, b, and c represent mole ratios of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

2. The method of claim 1, wherein sulfonating the provided oleo-furan compound comprises sulfonating the provided oleo-furan compound to produce each of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

3. The method of claim 1, further comprising:

selecting a sulfonating agent to control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

4. The method of claim 3, wherein selecting the sulfonating agent comprises selecting a first sulfonating agent to produce a first mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

5. The method of claim 4, wherein selecting the sulfonating agent comprises selecting a second sulfonating agent to produce a second mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4), and wherein the second sulfonating agent is different than the first sulfonating agent and the second mole ratio is different than the first mole ratio.

6. The method of claim 3, further comprising:

selecting at least one of a sulfonating agent loading, a solvent type, a sulfonation temperature, and a sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

7. The method of claim 6, wherein selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time comprises selecting each of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

8. The method of claim 6, wherein selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time comprises:

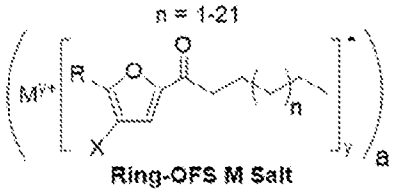
selecting a first sulfonation temperature and a first sulfonation reaction time to produce a first mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4), and

selecting a second sulfonation temperature and a second sulfonation reaction time to produce a second mole ratio a, b, and c of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4),

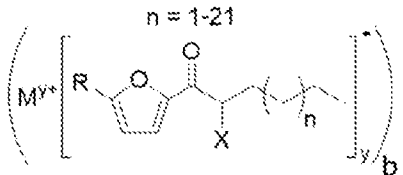
wherein the second sulfonation temperature is different than the first sulfonation temperature, the second sulfonation reaction time is different than the first sulfonation reaction time, and the second mole ratio is different than the first mole ratio.

9. The method of claim 1, further comprising:

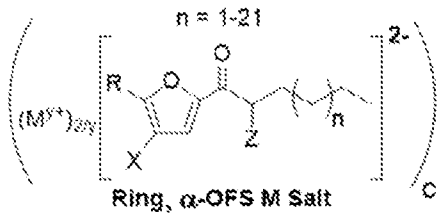
neutralizing the produced at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4) to produce at least two of a first neutralized oleo-furan sulfonic acid according to formula (5), a second neutralized oleo-furan sulfonic acid according to formula (6), and a third neutralized oleo-furan sulfonic acid according to formula (7):



(5),



(6),



(7),

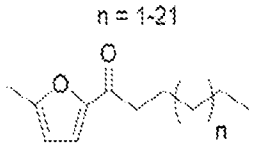
wherein a, b, and c represent mole ratios of the at least two of the first neutralized oleo-furan sulfonic acid according to formula (5), the second neutralized oleo-furan sulfonic acid according to formula (6), and the third neutralized oleo-furan sulfonic acid according to formula (7).

10. The method of claim 9, wherein neutralizing the produced at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4) comprises neutralizing each of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid

according to formula (4) to produce each of the first neutralized oleo-furan sulfonic acid according to formula (5), the second neutralized oleo-furan sulfonic acid according to formula (6), and the third neutralized oleo-furan sulfonic acid according to formula (7).

11. A method comprising:

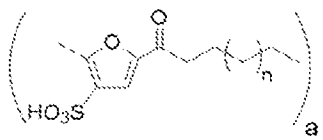
providing an oleo-methylfuran compound according to the formula (1):



Oleo-MethylFuran

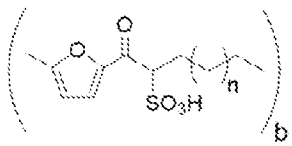
(1); and

sulfonating the provided oleo-methylfuran compound to produce at least two of a first oleo-methylfuran sulfonic acid according to formula (2), a second oleo-methylfuran sulfonic acid according to formula (3), and a third oleo-methylfuran sulfonic acid according to formula (4):



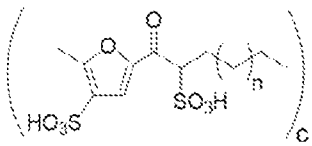
4-OMFS Acid

(2),



α-OMFS Acid

(3),



4,α-OMFS Acid

(4),

wherein n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and wherein a, b, and c represent mole ratios of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

12. The method of claim 11, wherein sulfonating the provided oleo-methylfuran compound comprises sulfonating the provided oleo-methylfuran compound to produce each of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

13. The method of claim 11, further comprising:

selecting a sulfonating agent to control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

14. The method of claim 13, wherein selecting the sulfonating agent comprises selecting a first sulfonating agent to produce a first mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

15. The method of claim 14, wherein selecting the sulfonating agent comprises selecting a second sulfonating agent to produce a second mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4), and wherein the second sulfonating agent is different than the first sulfonating agent and the second mole ratio is different than the first mole ratio.

16. The method of claim 13, further comprising:

selecting at least one of a sulfonating agent loading, a solvent type, a sulfonation temperature, and a sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

17. The method of claim 16, wherein selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time comprises selecting each of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time to further control selectivity for mole ratios a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4).

18. The method of claim 16, wherein selecting at least one of the sulfonating agent loading, the solvent type, the sulfonation temperature, and the sulfonation reaction time comprises:

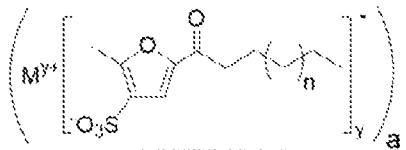
selecting a first sulfonation temperature and a first sulfonation reaction time to produce a first mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4), and

selecting a second sulfonation temperature and a second sulfonation reaction time to produce a second mole ratio a, b, and c of the at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4),

wherein the second sulfonation temperature is different than the first sulfonation temperature, the second sulfonation reaction time is different than the first sulfonation reaction time, and the second mole ratio is different than the first mole ratio.

19. The method of claim 11, further comprising:

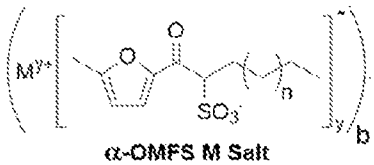
neutralizing the produced at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) to produce at least two of a first neutralized oleo-methylfuran sulfonic acid according to formula (5), a second neutralized oleo-methylfuran sulfonic acid according to formula (6), and a third neutralized oleo-methylfuran sulfonic acid according to formula (7):



4-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

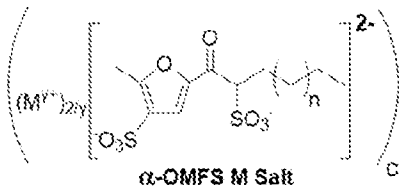
(5),



α-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

(6),



α-OMFS M Salt

M = Na^+, NH_4^+, Li^+, K^+, Ca^{2+}, Mg^{2+}

(7),

wherein a, b, and c represent mole ratios of the at least two of the first neutralized oleo-methylfuran sulfonic acid according to formula (5), the second neutralized oleo-methylfuran sulfonic acid according to formula (6), and the third neutralized oleo-methylfuran sulfonic acid according to formula (7).

20. The method of claim 19, wherein neutralizing the produced at least two of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) comprises neutralizing each of the first oleo-methylfuran sulfonic acid according to formula (2), the second oleo-methylfuran sulfonic acid according to formula (3), and the third oleo-methylfuran sulfonic acid according to formula (4) to produce each of the first neutralized oleo-methylfuran sulfonic acid according to formula (5), the second neutralized oleo-methylfuran sulfonic acid according to formula (6), and the third neutralized oleo-methylfuran sulfonic acid according to formula (7).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/80722

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C11D 1/12, C07D 307/02, C07D 307/64 (2023.01)
ADD. C07D 307/34 (2023.01)

CPC - INV. C11D 1/12, C07D 307/02, C07D 307/64
ADD. C07D 307/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PARK et al. "Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans", ACS Cent. Sci. 2016. 2, pp 820-824, especially: pg 821, Figure 2, 2-dodecanoylfuran, reaction pathway (ii); pg 821, col 2, para 2; supporting information, pg S6, para 1.	1,3-10
A	US 2020/0308475 A1 (HALLIBURTON ENERGY SERVICES, INC.) 1 October 2020 (01.10.2020), especially: para [0019], formula.	1,3-10
A	XIE et al. "Preparation of Methyl Ester Sulfonates Based on Sulfonation in a Falling Film Microreactor from Hydrogenated Palm Oil Methyl Esters with Gaseous SO3", Ind. Eng. Chem. Res. 2013. 52, pp 3714-3722, especially: pg 3714, col 1, para 1; pg 3715, Scheme 1; pg 3715, Table 1, methyl myristate.	1,3-10
A	US 2018/327375 A1 (CHRISTOPH KRUMM et al.) 15 November 2018 (15.11.2018), entire document.	1,3-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 April 2023 (07.04.2023)	MAY 01 2023
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/80722

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(see extra sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1,3-10

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 22/80722

--Box III - Lack of Unity--

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I+: Claims 1-20 directed to a method comprising: providing an oleo-furan compound according to the formula (1); and sulfonating the provided oleo-furan compound to produce at least two of a first oleofuran sulfonic acid according to formula (2), a second oleo-furan sulfonic acid according to formula (3), and a third oleo-furan sulfonic acid according to formula (4): wherein n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and wherein a, b, and c represent mole ratios of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). The method of claim 1 will be searched to the extent that it encompasses the first species of claim 1, wherein n is 1; R is H; and sulfonating the provided oleo-furan compound to produce a first oleofuran sulfonic acid according to formula (2), and a second oleo-furan sulfonic acid according to formula (3). It is believed that claims 1 and 3-10 encompass this first named invention, and thus these claims will be searched without fee to the extent that they encompass the first species of claim 1. This first named invention has been selected based on the guidance set forth in section 10.54 of the PCT International Search and Preliminary Examination Guidelines. Applicant is invited to elect additional methods of claim 1, wherein each additional compound elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected compound. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a method of claim 1, wherein n is 2; R is H; and sulfonating the provided oleo-furan compound to produce a first oleofuran sulfonic acid according to formula (2), and a second oleo-furan sulfonic acid according to formula (3) (i.e. claims 1 and 3-10).

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique method of claim 1, which is not required by any other invention of Group I+.

Common technical features:

The inventions of Groups I+ share the technical feature of a method comprising: providing an oleo-furan compound according to the formula (1); and sulfonating the provided oleo-furan compound to produce at least two of a first oleofuran sulfonic acid according to formula (2), a second oleo-furan sulfonic acid according to formula (3), and a third oleo-furan sulfonic acid according to formula (4): wherein n is an extended saturated alkyl chain from 1 to 21 carbon atoms in length, and wherein a, b, and c represent mole ratios of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4).

These shared technical features, however, do not provide a contribution over the prior art, as being obvious over the article entitled "Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans" by Park et al. (hereinafter 'Park') in view of the article entitled "Preparation of Methyl Ester Sulfonates Based on Sulfonation in a Falling Film Microreactor from Hydrogenated Palm Oil Methyl Esters with Gaseous SO3" by Xie et al. (hereinafter 'Xie').

Park teaches a method comprising: providing an oleo-furan compound according to the formula (1): wherein n is 7 and R is H (pg 821, Figure 2, 2-dodecanoylfuran); and sulfonating the provided oleo-furan compound to produce a first oleofuran sulfonic acid highly similar to formula (2) wherein X is H (pg 821, Figure 2, reaction pathway (ii)), but Park doesn't teach wherein n is 7; and R is SO3H (Park teaches the sodium salt) and Park doesn't teach at least two of a first oleofuran sulfonic acid according to formula (2), a second oleo-furan sulfonic acid according to formula (3), and a third oleo-furan sulfonic acid according to formula (4), thus Park also doesn't teach wherein a, b, and c represent mole ratios of the at least two of the first oleo-furan sulfonic acid according to formula (2), the second oleo-furan sulfonic acid according to formula (3), and the third oleo-furan sulfonic acid according to formula (4). However, the sulfonation reaction taught by Park uses SO3 (supporting information, pg S6, para 1, All prepared surfactant monomers (including reference standards such as 2-n-heptylfuran) was sulfonated and neutralized to make oleo-furan sulfonate surfactants (OFS-n, OFS-n-1/O, OFSn-2/2H5), sodium 2-R-furan-5-sulfonate (R = different alkyl chains), by the following method. The synthesized monomers (13 mmol) were added to a slurry of sulfur trioxide-pyridine complex (13 mmol) in anhydrous acetonitrile (12 mL)) and Xie teaches that sulfonation of similar long chain fatty acid esters using SO3 leads to sulfonation at the carbonyl alpha carbon atom (pg 3714, col 1, para 1, Methyl ester sulfonate (MES), an anionic surfactant prepared from natural renewable resources, such as vegetable oil, is considered to be the substitute for the petroleum-derived counterparts; see also pg 3715, Scheme 1; see also pg 3715, Table 1, methyl myristate) and it would have been obvious to a person having ordinary skill in the art to determine that the sulfonation reaction of Park also produced a second oleo-furan sulfonic acid according to formula (4) because the teachings of Xie suggest this. It would have also been obvious to combine Xie with Park because Park teaches a sulfonate derivative of a hydrophobic alkyl chain based detergent (pg 821, col 2, para 2, In this work, we replace the benzene moiety of LAS with biomass-derived furans20 to link polar and hydrophobic alkyl chains from the fatty acids of natural oils21 to form new oleofuransulfonate (OFS) surfactants, shown in Figure 1B, that can retain detergency without the need for additives such as chelants) and Xie also teaches a sulfonate derivative of a hydrophobic alkyl chain based detergent (pg 3714, col 1, para 1, Today, most of the main active matters added into commodities such as detergent, soap, shampoo, and facial cleanser come from petroleum-derived products... Methyl ester sulfonate (MES), an anionic surfactant prepared from natural renewable resources, such as vegetable oil, is considered to be the substitute for the petroleum-derived counterparts; see also pg 3715, Scheme 1; see also pg 3715, Table 1, methyl myristate). It would have been further obvious to prepare the neutral acid form of the salt of Park by routine experimentation in order to identify the compound which has the best properties for handling and formulation of the final detergent in the course of development and commercialization.

As said method was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the inventions of Group I+.

The inventions of Group I+ thus lack unity under PCT Rule 13.