

## Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans

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### Introduction.

Surfactants are amphiphilic molecules that improve wetting by lowering the surface tension. The molecular structure of a surfactant determines its efficacy and drives its properties; addition of carbons or branching in the linear hydrophobic chain can have dramatic effects in surfactant performance. Anionic surfactants constitute 50% of the \$30 billion global surfactant industry and are widely used in household detergents, and personal care products [1]. Linear alkylbenzene sulfonates (LAS) are widely used due to their low cost and high detergency. Current LAS production methods rely on toxic catalysts and petrochemical-based constituents, such as benzene and long chain hydrocarbons. The reaction has low selectivity to the prescribed linear structure thereby rendering minimal control over the desired composition and properties [2]. Additionally, calcium ions in hard water bind to LAS causing it to precipitate from the solution thereby making it unusable.

In this work, we propose a novel, renewable pathway to produce biodegradable oleo-furan sulfonate (OFS) surfactants with strong detergency, and good solubility made from biomass-derived feedstocks, such as furan and fatty acid via Friedel-Crafts acylation, aldol condensation, catalytic hydrogenation and sulfonation that outperform LAS in surfactant properties such as stability in hard water

### Materials and Methods

Acylation, hydrogenation and aldol condensation reactions were carried out in a 100 mL, high-pressure, high-temperature Parr reactor (model 4598HTHP with a 4848-temperature controller) while sulfonation was performed in standard laboratory glassware. Al and Sn MWW and SPP zeolite catalyst were synthesized using an existing method [3]. The reaction products were identified via NMR spectroscopy (Bruker AX400, 400 MHz) and GC-MS (Agilent 7890A connected with Triple-Axis MS detector, Agilent 5975C) equipped with a HP-5 column and a flame ionization detector (FID).

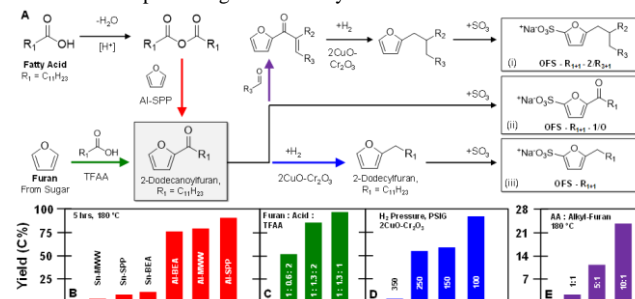
### Results and Discussion

OFS surfactants were synthesized by linking biomass-derived furan via Friedel-Crafts acylation to triglyceride-derived long chain fatty acids. Palm and soybean oil-derived fatty acids can be converted to an anhydride using short chain anhydrides which can then react with furan in the presence of a heterogeneous zeolite catalyst. The results obtained for the reaction of lauric anhydride with furan show that different pore sizes, structures and acidity of

zeolites result in varying acylation activity (Figure 1B). While the yield of acylated furans was a low 11% over a Lewis acid zeolite such as Sn-BEA, a hierarchical porous Brønsted acid zeolite such as Al-SPP yielded ~90% after a 5 h reaction at 180°C. Alternatively, the fatty acid can also be made to undergo an instantaneous acylation reaction with furan using trifluoroacetic anhydride (TFAA) resulting in over 95% yield of 2-dodecanoylfuran (Figure 1C). The ketone functionality can be eliminated via selective hydrogenation using copper chromite (2CuO-Cr<sub>2</sub>O<sub>3</sub>) to produce 2-dodecylfuran with 90% yield (Figure 1D). Additionally, a third class of branched alkylfurans was prepared by aldol condensation of 2-dodecanoylfuran with acetaldehyde as depicted in Figure 1E. The remaining furan alpha carbon in these three classes of molecules (ketone, straight chain and branched, as shown in Figure 1A) were sulfonated using sulfur trioxide-pyridine complex. Evaluation of surfactant performance of OFS revealed hundredfold better detergency and stability in hard water conditions in comparison with LAS [4].

### Significance

The proposed technology differs from the existing LAS production process in that the acylated products do not easily isomerize or form side products, thereby resulting in high selectivity to the desired surfactant. This unique advantage enables synthesis of number of application-specific surfactants with high yield. The synthesis of OFS molecules is, highly tunable and selective where the number of carbon atoms in the linear or branched chain can be easily varied without compromising on reaction yields to achieve desired surfactant properties.



**Figure 1.** Furan acylation to renewable OFS surfactants A) Reaction sequence for synthesis of OFS B) Acylation using hierarchical zeolites, C) Acylation using TFAA, D) Hydrogenation of 2-dodecanoylfuran, E) Aldol condensation of 2-dodecanoylfuran with acetaldehyde.

### References

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