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Quantifying fat, oil, and grease deposit formation kinetics

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ABSTRACT

Fat, oil, and grease (FOG) deposits formed in sanitary sewers are calcium-based saponified solids that are responsible for a significant number of nationwide sanitary sewer overflows (SSOs) across United States. In the current study, the kinetics of lab-based saponified solids were determined to understand the kinetics of FOG deposit formation in sewers for two types of fat (Canola and Beef Tallow) and two types of calcium sources (calcium chloride and calcium sulfate) under three pH (7 ± 0.5, 10 ± 0.5, and ≈ 14) and two temperature conditions (22 ± 0.5 and 45 ± 0.5 °C). The results of this study displayed quick reactions of a fraction of fats with calcium ions to form calcium based saponified solids. Results further showed that increased palmitic fatty acid content in source fats, the magnitude of the pH, and temperature significantly affect the FOG deposit formation and saponification rates. The experimental data of the kinetics were compared with two empirical models: a) Cotte saponification model and b) Foubert crystallization model and a mass-action based mechanistic model that included alkali driven hydrolysis of triglycerides. Results showed that the mass action based mechanistic model was able to predict changes in the rate of formation of saponified solids under the different experimental conditions compared to both empirical models. The mass-action based saponification model also revealed that the hydrolysis of Beef Tallow was slower compared to liquid Canola fat resulting in smaller quantities of saponified solids. This mechanistic saponification model, with its ability to track the saponified solids chemical precursors, may provide an initial framework to predict the spatial formation of FOG deposits in municipal sewers using system wide sewer collection modeling software.

1. Introduction

Municipalities are facing increased challenges in establishing maintenance requirements in their Sewer System Management Plans (SSMP) based on identifying collection system pipes that are subjected to frequent accumulation of fat, oil, and grease (FOG) deposits (Tupper, 2010). FOG deposits are known as calcium based saponified solids and have been implicated in almost a quarter of the sanitary sewer overflows (SSOs) throughout the United States. However, municipalities continue to struggle with clearly associating the formation of FOG deposits in these sewer collection pipes with the wastewater discharge characteristics of food service establishments (FSEs) beyond their released amount of total oil and grease (Report to Congress, 2004). Clear identification of factors that influence the rate of FOG deposit formations in certain pipe segments would allow municipalities to impose new FOG discharge limits, impose alternative grease interceptor pump out cycles, or investigate new ways to assist the FSEs in improving their cleaning procedure. Therefore, a detailed study is needed to quantify how different source and environmental factors in sewer systems and/or FSEs impact the rates of FOG deposit accumulation. Once these rates have been quantified, a model could be developed that can capture the kinetics of FOG deposits and can potentially be incorporated in system wide municipal sewer collection system models for use by pretreatment managers.

He et al. (2011) demonstrated that FOG deposits are similar to calcium-based saponified solids first hypothesized by Keener et al. (2008). These saponified solids are products of a chemical reaction between free fatty acids released during fat hydrolysis and calcium ions. Sodium and potassium alkalis have traditionally been used by researchers in fat saponification (Smith, 1932). However, calcium has been found as the predominant metal in FOG deposits of sewer systems (Keener et al., 2008; He et al., 2011, 2013; Williams et al.,

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2012; Iasmin et al., 2014; Pastore et al., 2015). Conventional fats that are associated with the cooking process in FSE range from saturated (palm oil and animal derived fats such as beef tallow, butter, and chicken fats) to mono-unsaturated/poly-unsaturated fats (cooking oils such as canola oil, corn oil, olive oil, soybean oil, and vegetable oils). It was expected that such fat sources would produce a range of fatty acids within these saponified solids. However, Keener et al. (2008) found palmitic as the predominant fatty acid (i.e., saturated) in FOG deposits which was later observed by He et al. (2011) while producing laboratory based FOG deposits with grease interceptor (GI) effluent wastewater and the addition of calcium chloride.

Recently, Iasmin et al. (2014) determined that some source and environmental factors, i.e., types of fats used in FSEs (saturated vs. unsaturated), types of calcium sources available in sewer systems, and the environmental conditions, i.e., pH and temperature in sewer systems affect the physical, chemical, and rheological properties of FOG deposits. Iasmin et al. results showed that fatty acid profiles of the calcium-based saponified solids produced under alkali driven hydrolysis were identical to the fatty acid profiles of the source fats. Their results also suggest that calcium content in the FOG deposits may depend on the solubility limits of the calcium sources that are influenced by the pH and temperature conditions in the sewer system. These different source and environmental conditions may have a significant impact on the rate of FOG deposit formation, which was not assessed in Iasmin et al. (2014). Therefore, to identify potential susceptible locations for FOG deposit related blockages in sewer collection systems, the kinetics of FOG deposits are needed based on variable source and environmental factors uncovered in Iasmin et al. (2014).

Literature reviews on models that relate to saponification reactions have reported an autocatalytic nature of these reactions and that their kinetics tends to follow an “S”-shaped curve (Smith, 1932; Jones, 1958; Poulenat et al., 2003; Cotte et al., 2006). Cotte et al. (2006) proposed an empirical saponification model that characterizes the entire experimental ‘S’ shape kinetics of triolein saponification by lead salts, at temperatures ranging from 100 to 180 °C. Cotte et al. showed good agreement between the predicted and experimental aqueous PbO data. Fat crystallization empirical model proposed by Foubert et al. (2002) was also found to follow an “S” shaped curve for crystallization kinetics. Due to the “S” shaped profiles uncovered by both Cotte et al. (2006) saponification and Foubert et al. (2002) crystallization kinetics, both models have the potential to capture the calcium-based saponification kinetics of FOG deposits in sewer systems. While these empirical models may give plausible information related to the formation rate of FOG deposits, neither model tracks the rate of fat hydrolysis (i.e., the release of fatty acids that would then participate in the saponification reaction). Therefore, an additional part of this study was to develop a mechanistic model for the production of saponified solids. Overall, the objectives of this research were: 1) to determine the kinetics of calcium-based saponified solids, 2) to evaluate environmental conditions that influence the rate of formation, and 3) to evaluate and develop a model that captures the experimental saponification kinetics data.

2. Experimental

2.1. Formation of calcium based saponified solids under laboratory conditions

An alkali-driven saponification process was followed to develop the calcium based fatty acid salts. In brief, an aqueous solution of calcium chloride/calcium sulfate was prepared and brought down to room temperature (22–25 °C). The liquid/melted-solid fat (Canola or Beef tallow) was then added to the aqueous calcium solution and mixed for eight hours under three different pH (7 ± 0.5, 10 ± 0.5, and ≈ 14) and two different temperature conditions (25 and 45 °C). Kinetic samples were collected for eight hours, at 15 min intervals for the first hour and at 30 min intervals till the eighth hour to capture the kinetics of the calcium-based saponified solid formation. The spectral data of the kinetic samples were subsequently obtained with a Digilab FTS-6000 Fourier Transform Infrared (FTIR) spectrometer with a mounted crystallized Zinc-Selenide (ZnSe) sampling attachment (4000–520 cm^{-1}; Pike Technologies Inc., MIRacle™ Single Reflection ATR). The data was analyzed with the Bio-Rad Win-IR Pro software version 2.97. OriginPro 8.1 was used for baseline correction, peak identification, and computation of absorbances of the characteristic bands (Pro, O. 8., 2007). Additional information can be found in Iasmin et al. (2014).

2.2. Computation of fraction of saponification using FTIR-ATR analysis

The quantity of saponified solids was measured following a modified equation of Poulenat et al. (2003) for relative absorbance of signature calcium-based saponified solid bands as described in Iasmin et al. (2014). Saponified solid fraction was computed following Equation (1) in which all the characteristic saponification bands (the carboxylate ion symmetric stretching vibration, between 1300 and 1420 cm^{-1}; the carboxylate ion asymmetric stretching vibration, between 1550 and 1610 cm^{-1}; and the metal–oxygen bond vibration, around 670 cm^{-1}) were incorporated.

$$Fraction\,of\,saponification = \frac{Absorbance\,in\,(near\,670\,cm^{-1} + between\,1300\,and\,1420\,cm^{-1} + between\,1550\,and\,1610\,cm^{-1})}{Absorbance\,in\,(near\,670\,cm^{-1} + between\,1300\,and\,1420\,cm^{-1} + between\,1550\,and\,1610\,cm^{-1} + 1745\,cm^{-1})} \tag{1}$$

2.3. Potential saponification models and evaluation

2.3.1. Empirical saponification models

In Cotte et al. (2006)'s saponification model, a two-step reaction process for saponification with Lead oxide (PbO) was proposed that involved: a) a slow dissolution of metal salt (L) in an aqueous solution and b) a reaction between the dissolved metal species (D) and the oil (O) to form saponified solids (S) and an alcohol (A) by-product (Equations (2) and (3)).

$$L \rightarrow D(\mathrm{k}_1) \tag{2}$$

$$D + O \rightarrow S + A(\mathrm{k}_2) \tag{3}$$

The final differential equation for the formation of saponified solids was described as follows: