Pelargonic Acid in Enhanced Oil Recovery

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ABSTRACT: Oxidation of monounsaturated fatty acids, such as erucic and oleic acids, results in the formation of dibasic fatty acids, such as brassylic and azelaic acids. Dibasic acids find many industrial applications. Pelargonic acid is the co-product of the process. Expanded use of dibasic acids would require an expansion in the existing and possibly new uses for pelargonic acid and its derivatives. In this study, the potential for using pelargonic acid in enhanced oil recovery is investigated. Experimental results are presented for the enhanced oil recovery by waterflooding with the aid of a surfactant. *In situ* formation of surfactant at the oil-water interface vs. the formation of surfactant in the floodwater prior to injection is examined.
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KEY WORDS: Enhanced oil recovery, fatty acids, oleic acid, pelargonic acid, surfactants.

Unsaturated fatty acids are the primary fatty acid components of most vegetable oils. Monounsaturated fatty acids, such as oleic and erucic acids, are major components of soybean and crambe oils, respectively. The dibasic acids, such as azelaic, are produced commercially by oxidative cleavage of monounsaturated fatty acids according to ozone oxidation chemistry (1–3) or other oxidation techniques (4). Azelaic acid finds industrial applications as plasticizers for polyvinyl chloride, lubricants, and polymer intermediates for polyamides, polyesters, and polyurethanes. Brassylic acid, which is the dibasic acid product of the oxidative cleavage of erucic acid, is produced in limited quantities but has a lot of potential for large-scale industrial applications, particularly in nylons 1313 due to improved properties over nylon 66. Low water absorption makes these nylons preferred over conventional nylons where conditions of high humidity affect properties such as tensile strength, elongation, toughness, and electrical conductivity (5). Mixed diesters of azelaic and brassylic acids, prepared from crambe oil, have been reported to be excellent plasticizers for polyvinyl chloride at low temperatures (6,7).

Pelargonic (nonanoic) acid is the co-product of oxidative cleavage of oleic and erucic acids. While there are existing applications for pelargonic acid, a significant increase in availability, resulting from expanded use of azelaic and brassylic acids and their derivatives, would require expansion in existing and possibly new uses for pelargonic acid. In this study, a brief review of the existing and potential applications for pelargonic acid is presented. Then, the potential for pelargonic acid in enhanced oil recovery (EOR) is investigated. Results of the experimental investigations indicate that secondary oil recovery is significantly improved when a surfactant, such as a long-chain fatty acid, is used. Furthermore, the results reveal that pelargonic acid is as effective as longer-chain fatty acids, such as oleic, palmitic, and stearic acids.

Pelargonic acid uses. Pelargonic acid finds a number of industrial applications in lubricants, cosmetics, and metalworking fluids. Pelargonic acid is among the principal raw materials used in synthetic lubricants (8). With few exceptions, in most applications pelargonic acid is used in the form of a derivative, such as mono-, di-, or polyolesters. The last group offers high thermal and oxidative stability, which is most desirable for lubricants. Ester lubricants find a variety of applications, particularly in gas turbines.

Fatty acids and their derivatives are widely used in cosmetic formulations. However, use of short-chain fatty acids, such as pelargonic acid, is limited and is used primarily in producing derivatives for cosmetics.

Pelargonic acid, when reacted with caustic or amines, forms soap, which is used in the formulation of synthetic nonmineral-oil-based metalworking fluids (9). These synthetic fluids, which are made from a number of organic compounds, will provide wetting, lubricity, and corrosion protection, as well as cooling in metalworking.

In the formulation of writing ink, pelargonic acid has been demonstrated to improve properties, such as fast drying, low viscosity, low degree of feathering, and good nibbability (10). α-Bromo pelargonic acid has been used as one of the active ingredients in the formulation of disinfectants (11). In the processing of synthetic fibers, dipelargonic esters of ethoxylated arylphenols as additives with organic industrial fluids increase high-temperature stability of such fluids, which is most desirable for their application (12).

EOR. EOR usually refers to the recovery beyond primary production and waterflooding. The objective is to facilitate recovery of more than 70% of the oil, which is normally left in the reservoir after primary and secondary (pressure maintenance and waterflooding) methods.

Due to variations in the nature of the reservoirs and the oil properties, there has been a whole range of unconventional and usually costly and complex EOR techniques, only a few of which have proven to be successful in field studies at commercial scale. Total EOR production in 1992 was 760,000 barrels per day, which is about 10% of the total U.S. production (13).

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In general, the EOR methods are broadly divided into thermal and nonthermal methods, depending on whether heat is employed in some form. Nonthermal EOR methods can be classified into chemical and miscible processes. Among many miscible processes that have been proposed, the carbon dioxide and hydrocarbon processes have been the most promising and account for about 33% of total EOR production (13). Chemical methods, such as surfactants, polymer and caustic, or alkaline floodings, have had limited success but hold a lot of promise for the future (14).

Surfactant flooding. The main objective in surfactant flooding is to reduce the interfacial tension between oil and water. Over the years, many advances have been made in this area, notably in the use of petroleum sulfonates and *in situ* formation of a surface-active agent (15).

In surfactant waterflooding, the reservoir is flooded with a water–surfactant mixture. The problem with this method is that the water that is already in the reservoir is replaced by the floodwater and forms a bank between the displaced oil and the injected floodwater. The result is that the surfactants do not reach the trapped oil and are not able to reduce the interfacial tension; nor is it possible to prevent trapping of the oil. This problem can be circumvented by formation of the surface-active agent *in situ* at the oil–water interface. Therefore, instead of introducing the surface-active agent in the water used in flooding, the surface-active agents are formed at the oil–water interface. This is done by introducing through an injection well and into the oil phase of a subsurface reservoir a solution of the first reactant mixed in the oil previously recovered from the same reservoir, and then injecting water containing the second reactant into the subsurface reservoir. Upon contact of the two phases, the surface-active agent is formed at the interface (15).

EXPERIMENTAL PROCEDURES

In this study, the effectiveness of pelargonic acid as a substitute for longer-chain fatty acids, such as oleic, palmitic, and stearic acids, in enhanced oil recovery is investigated. A 1 N sodium chloride solution, which was buffered to a pH of about 8.5 with sodium hydroxide and boric acid, is used in the floodwater to provide the sodium ion for the formation of the surfactants. A series of experiments was performed to investigate the effectiveness of oleic and pelargonic acids relative to one another and also to the situation where no surfactant was used. *In situ* formation of surfactant vs. its formation in the floodwater prior to flooding was also investigated. Four EOR experiments were performed. Three replicates were performed for each experiment. The four recovery experiments were: (i) using no surfactants, (ii) using oleic acid in the oil phase, (iii) using pelargonic acid in the oil phase, and (iv) using pelargonic acid in the flooding water.

Apparatus. A glass tube 2.5 feet long and 1.5 inches i.d. was used in all experiments. This tube was packed with 35–50 mesh sand. A fritted glass disk was installed at the lower end of the tube to keep the sand in place. Pumping was performed by a Pulsatran metering pump (E series; Pilsafeeder, Rochester, NY) with a maximum capacity of 20 GPD. Tygon vacuum/pressure tubing was used to connect the components. The flow diagram for the apparatus is shown in Figure 1.

Raw materials. The crude oil (U.S. Sweet Crude) was provided by Conoco Oil Company (Bartlesville, OK). Oleic and pelargonic acids were purchased from Aldrich Chemical Company (Milwaukee, WI) in purities of 90 and 96%, respectively. Sodium chloride with purity of 99% was purchased from Sigma Chemical Company (St. Louis, MO). The sand packing for the tube was an ordinary utility sand, which was classified in the 35–50 mesh range.

Effect of impurities. Although the impurities in oleic and pelargonic acids are not listed by the manufacturer, they are expected to be other fatty acids. This is due to the fact that a mixture of fatty acids from the natural sources of triglycerides (oil and fat) are involved in their manufacturing. Therefore, most impurities are expected to form surfactants and have an effect parallel to the main fatty acid being considered. In analysis of the results, it is assumed that the effects of impurities are insignificant.

Experimental procedures. The void fraction of the packed column was measured prior to the EOR experiments. This was done by measuring the volume of the tube once when it was empty and again when it was filled with sand. The ratio of the latter to the former volume is the void fraction. The void fraction was 0.41. Water was used in the volumetric measurements.

The *in situ* EOR experiments with pelargonic and oleic acids were performed according to the following procedures. The column was packed with sand. A 1 N aqueous solution of sodium chloride was pumped into the column. Pumping of the material into the column was always from the bottom

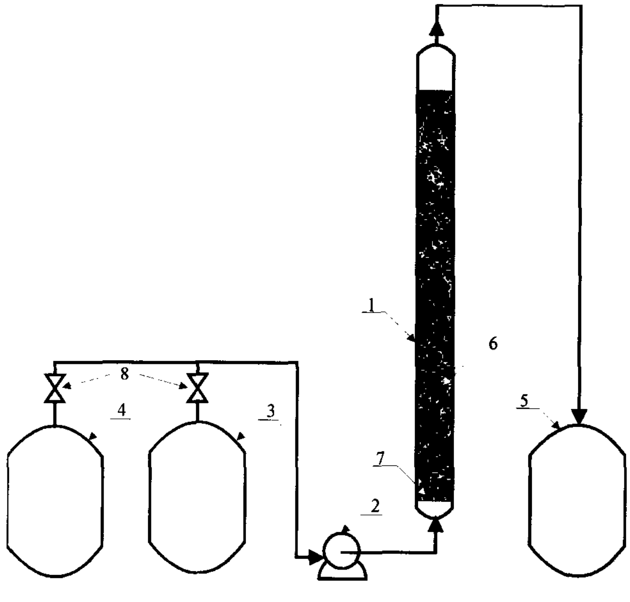

FIG. 1. Schematic diagram of the apparatus for enhanced oil recovery experiments. (1) packed column; (2) metering pump; (3) source tank for crude oil; (4) source tank for sodium chloride solution; (5) collection tank; (6) sand; (7) fritted glass; and (8) valves.

opening. This was continued until the sand was totally saturated with this solution. A solution of 3.0% by volume of fatty acid in crude oil was then pumped into the column. The exact volume of the oil–acid solution introduced into the column was measured with the metering pump. The column was then flooded with a 1 N solution of sodium chloride solution, which was buffered to a pH of about 8.5, with sodium hydroxide and boric acid. The total volume of the floodwater was equal to 15.4 times the pore volume, at a rate of 20.7 ft/day. The waterflooding forced some of the crude oil out of the column along with the flood solution. This solution was collected in a container. The oil and water phases were separated, and the volume of the recovered oil was recorded.

The EOR experiments involving pelargonic acid in the flooding water were performed according to a similar procedure except that the pelargonic acid, in an amount equal to the volume of the pelargonic acid which was used in the *in situ* EOR experiments, was added to the floodwater solution. The surfactant, which is formed in the floodwater solution, was mostly miscible in the salt solution. However, the solution was kept under continuous agitation during pumping.

The experimental procedures for the experiments involving no surfactants were identical, except that no acid was added to the oil or to the floodwater solution.

RESULTS AND DISCUSSION

The results of the EOR experiments are tabulated in Table 1. The experimental results show that *in situ* formation of surfactants improves secondary oil recovery. Furthermore, the results indicate that the recovery with pelargonic acid is significant and is comparable to the recovery with longer-chain fatty acids such as oleic acid. There is about 10% increase on the recovery for pelargonic acid and about 13% increase when oleic acid is used.

The results also reveal that oil recovery in a waterflooding process in which the surface-active agent is formed in the floodwater is no different from that which normally occurs in a waterflooding operation in which no surface-active agent is present in the floodwater.

TABLE 1
Results for Enhanced Oil Recovery Experiments

Run description	Oil introduced initially (V_i), mL	Oil recovered (V_r), mL	Percentage recovery (V_r)/(V_i) • 100
No surfactant	300	125	42
No surfactant	300	132	44
No surfactant	280	126	45
C_9 (in oil)	270	150	56
C_9 (in oil)	275	147	53
C_9 (in oil)	285	148	52
C_{18} (in oil)	280	161	57
C_{18} (in oil)	285	158	55
C_{18} (in oil)	290	168	58
C_9 (in floodwater)	275	119	43
C_9 (in floodwater)	275	115	42
C_9 (in floodwater)	275	123	45

The experimental results indicate that pelargonic acid forms a good surface-active agent in the EOR process, but the economics of the process still appear to favor the use of oleic acid due to lower cost. According to the chemical price index (16), pelargonic acid is more expensive than oleic acid ($0.71/pound for oleic compared to $1.10/pound for pelargonic) and may still be more attractive for EOR. However, expanded use of azelaic and brassylic acids may favor lower market value for pelargonic acid due to increase in availability, which may make it more competitive with oleic acid.

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