Novel Surfactants for Enhanced Oil Recovery

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ABSTRACT

Despite the advent of numerous alternative energy technologies and fuels, the U.S. will continue to rely on oil, especially from imported sources, to satisfy its energy demand for the foreseeable future. As there is little debate among oil industry experts that nearly 400 billion barrels of oil lies "stranded" in the U.S., the challenge to improve domestic energy security is to develop state-of-the-art Enhanced Oil Recovery (EOR) technologies with the performance to cost effectively extract this stranded oil [1].

Of all the potential EOR technologies, CO2EOR is the most successful and widely practiced. Novomer is developing breakthrough surfactant technology that can significantly enhance CO2EOR with the potential to dramatically improve CO2EOR yields. In accomplishing this goal, this technology also enables the potential for significant CO_2 sequestration.

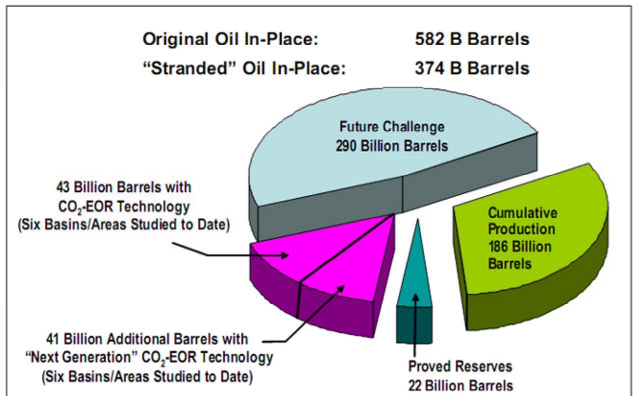
Keywords: enhanced oil recovery, carbon dioxide, surfactant, catalyst, novomer

BACKGROUND

In 2008 the United States average consumption of crude oil was 14.7 million barrels per day. Of that, 5.0 million barrels per day were produced domestically, and 9.7 million barrels per day were imported, with 6.0 million barrels per day coming from OPEC sources. Collectively, the purchase of imported oil represents an outflow of nearly $680 Billion per year or 3% of the total goods imported by the U.S. in 2008. The Administration's Energy and Environment Agenda has set the goal to save more oil than the U.S. currently imports from the Middle East and Venezuela combined (more than 3.5 million barrels per day) within 10 years. [2]

In 2007, the United States had proven oil reserves totaling 23 billion barrels of oil from which 1.8 billion barrels annually were produced. Proven reserves are defined as "Proved reserves of crude oil (as of December 31 of the report year) and are the estimated quantities of all liquids defined as crude oil, which geological and engineering data demonstrate with reasonable certainty to be recoverable in future years from known reservoirs under existing economic and operating conditions".

Consequently, proven reserves depend not only on the amount of oil in a deposit (defined as OOIP or Original Oil In Place) but also having an economic way to recover it for use. In a 2008 study presented to the DOE, Advanced Resources International (ARI) calculated that the inefficiency of historic oil producing practices has left 400 billion barrels of oil ''stranded" in already identified oil wells in the United States. [3] Identifying and implementing economic ways to recover that stranded oil and reduce oil imports, therefore, has been a goal of industry and government over the past three decades.



Estimates of Stranded Oil – NPC Public Data Base, Maintained by DOE/FE (2004)

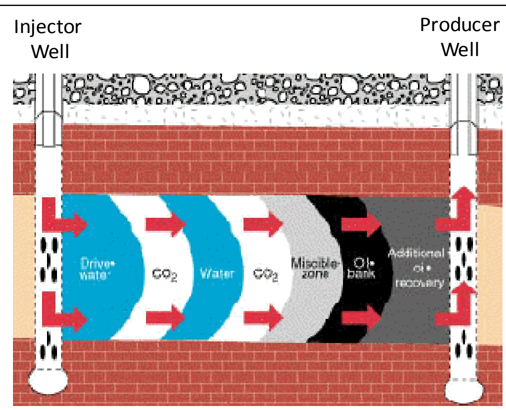
Oil production takes place essentially in three phases. Primary recovery is oil that is forced to the surface by the natural pressure released by the initial drilling operation. Typically 12% to 15% of a deposit's OOIP is captured at this stage. Secondary recovery uses water flooding to force oil from the deposit and typically recovers an additional 6% to 30% of the OOIP. The vast majority of oil fields will utilize both primary and secondary recovery and capture 20-40% of OOIP. Tertiary recovery – or EOR (Enhanced Oil Recovery) – utilizes other complex and more costly methods to capture an additional 10% to 40% of OOIP beyond primary and secondary recovery. The net result is a total recovery of 30% to 80% of the OOIP, **leaving 20% to as much as 70% of the OOIP stranded.**

There are many types of EOR, but the low cost and effectiveness of gas forms of EOR has created growth while others methods (e.g. thermal, chemical) have declined. Of the 1.8 billion barrels of oil produced in 2007, about 240 million barrels were produced by EOR. The most rapidly growing form of EOR are Carbon Dioxide Floods, or

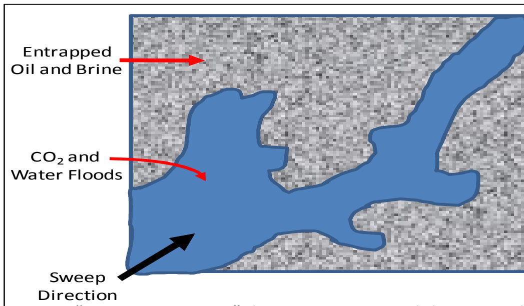
CO2EOR, which has grown since its inception in 1984 to producing over 86 million barrels per year. [4]

The basic features of CO2EOR that enable its growth include; CO_2 is miscible at the low pressures in most well environments (versus nitrogen or methane), cheaper and more plentiful than other potential miscible gases (LPG, enriched hydrocarbon gas), and has a density (in dense or supercritical phase) close to that of other reservoir fluids (oil, water). When injected into an oil deposit with a porous rock substrate, CO_2 dissolves (miscibility effect) some of the oil components causing swelling that reduces density and the oils viscosity. This reduces interfacial tension and enables the oil to be more easily removed from the pores with subsequent water washes and recovered.

The problem with CO_2 is that it is highly mobile and, instead of acting on oil filled channels, it seeks the path of least resistance (unfilled channels) and, thus, a significant portion of the injected CO_2 escapes out the producing well without recovering any additional oil. This phenomenon, called viscous fingering, greatly increases the cost per barrel recovered. *"The major technical challenge isn't finding reservoirs amenable to CO_2 floods - - it's being able to control proper mobility and proper sweep of the injected gas. Most CO_2 floods entail injecting a large slug of CO_2 followed by injection of water which drives the CO_2 - - to maximize sweep efficiency. Modifying CO_2 viscosity is critical because differences in CO_2 viscosity and density relative to the crude oil-in-place can set the stage for premature breakthrough of the gas."* [5] Despite this drawback, CO2EOR is seen as a technology that can significantly impact the production of oil in the United States and reduce our dependence on foreign oil if "state-of-the-art" technologies can be developed.



Water Alternating Gas (WAG) CO2EOR Process



"Viscous Fingering" due to poor CO_2 Mobility Control

Although "technically recoverable", just as important is that the combination of oil price and recovery cost enable economic recovery. It is estimated that 40 to 90 billion barrels of the stranded oil would be economically viable if such "state-of-the-art" CO2EOR technology were utilized, CO_2 was readily available at \$35 to \$60 per MT, and oil was priced at \$50 to \$90 per barrel. If one makes the assumption that the oil would be produced and delivered over a forty year period of time – typical lifespan of an oil well - that would be 2.0 to 3.3 million barrels per day of new oil production. This would significantly impact the Administration's goal for the reduction of foreign oil. [6]

Region/State	Technically Recoverable (Billion Barrels)	Existing CO2-EOR Production/ Reserves	Incremental Technically Recoverable (Billion Barrels)
1. Permian (W TX, NM)	17.8	-1.9	15.9
2. Texas, East/Central	17.6	-	17.6
3. Alaska	12.4	-	12.4
4. Mid-Continent (OK,	10.7	-0.1	10.6
5. Gulf Coast (AL, FL,	7		7
6. California	6.3	-	6.3
7. Louisiana Offshore	5.8	-	5.8
8. Other (IL, MI, MT, ND, SD, WV, OH, KY,	5.3	-	5.3
9. Rockies (CO, UT,	4.2	-0.3	3.9
total	87.1	-2.3	84.8

Technically recoverable oil with State-of-the-Art CO2EOR

The technique of using CO2 mobility control to assure its contact with the oil is well documented in the literature. One key area of research for overcoming this issue has been to modify the viscosity of the CO2. In particular, a highly effective method identified for the accomplishing of this task is the creation of CO2 foam that forms within the rock formation itself. The foam enters the pores of the rock of the formation containing only brine. The foamed CO2 significantly increases the resistance for more CO2 to enter, in essence "blocking off" these pores. The foam does not form in the oil containing pores and the CO2 becomes miscible with the oil - accomplishing its purpose - and enables the oil to be swept to the producer well and recovered.

The current state of the art approach utilizes a family of alcohol propoxy sulfates, which are anionic surfactants.

They are injected into the wells as "surfactant slugs" made up of brine and surfactant of up to approximately 3% the brine weight. The "surfactant slug" will then be followed up by several days of injection of brine or a "brine push".

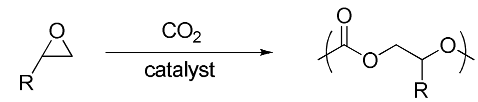
In practice, however, these ratios are difficult to maintain. The huge volumes of brine and surfactant involved in a "surfactant slug" can be potentially lost in "thief zones" (oil free zones) where large fractures or fissures exist. This potentially limits the approach for use only in carbonate rock formations with uniform pores. In addition, anionic surfactants suffer from adsorption losses as they are readily attracted to the surface of carbonate rock formations: "Surfactant absorption on the reservoir minerals presents a potential problem because abstraction of the surfactant from the dispersion will destabilize the dispersion……Further, because the injected surfactant is a major portion of the overall cost of the project, its loss should be minimized to optimize process economics"[7]

Field trials of anionic surfactants have experienced losses as high as 90% of the injected surfactant. The surfactant that is adsorbed to the rock formation is not available to stabilize the, rendering this approach unproductive and uneconomical. This issue has been partially addressed by pre-treating the rock formations with alkaline materials such as sodium carbonate, but this represents an additional process and cost with varying effectiveness and may even be damaging to some non-carbonate rock formations.

Previous work has suggested a different surfactant approach: create a non-ionic CO2 soluble surfactant that can be injected in the CO2 portion of the flood. This makes the risk of loss to thief zones minimal (anionic surfactants will not adsorb to the formation) and significantly less surfactant will be required given the lower quantities of CO2 injected. Although the approach itself is accepted, the difficulty has been in actually designing and producing an economic surfactant that enables these advantages. From the description of this problem in 1998 until today, this has been an important target for surfactant design within the enhanced oil recovery community. To date, however, only a few surfactants identified fit this description, all containing fluorocarbons which are both expensive and environmentally problematic.

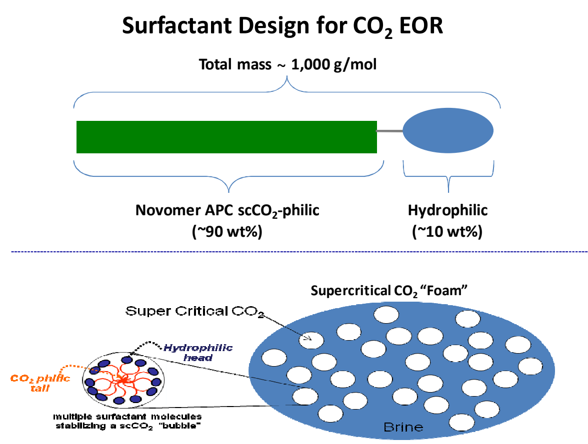
NOVOMER ADVANCES

Novomer Inc. has developed a patented a range of surfactants leveraging its proprietary APC technology. The key to the technology is the APC molecule which, when functionalized with a polyether, can create a family of surfactants with the unique ability to be soluble in CO2 and be hydrophilic. Novomer is unique in its ability to produce low cost Aliphatic Polycarbonates through patented catalyst technology and the use of carbon dioxide as a primary raw material.



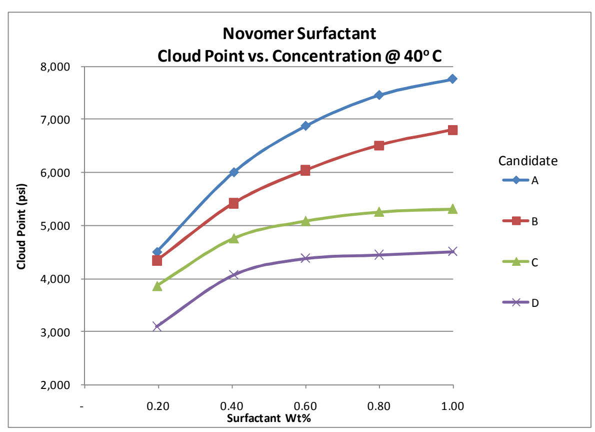
Epoxide Aliphatic Polycarbonate

The aliphatic carbonate side of the molecule readily dissolves in CO2 while the polyether is soluble in water. By combining these two components in a single molecule, the surfactant can be dissolved in CO2 and used during the CO2 injection. As the molecule is non-ionic, the issue of adsorption to the rock formation is eliminated and the molecule can be produced economically (approximately 45% of the APC portion is composed of waste CO2).



In addition, its architecture is easily modified in both chain length and hydrophilic end groups to meet the multiple requirements of various oil well formations and rock structures.

Initial CO2 solubility and foam testing has already demonstrated the potential of this technology. This technical breakthrough has been enabled by Novomer's unique ability to produce low cost aliphatic polycarbonates from CO2 using patented catalyst technology.



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