

## 'Green' Frac Fluid Chemistry Optimizes Well Productivity, Environmental Performance

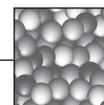
By Kevin Fisher

HOUSTON—Long before the media scrutiny and environmental activism surrounding hydraulic fracturing surfaced, the industry was seeking to develop environmentally friendly fracturing fluids. The "Holy Grail" objective of frac fluid research and development long has been technology that is natural, biodegradable, and intrinsically safe for the environment while simultaneously enhancing fracture effectiveness and long-term well performance.

A prime example of the type of next-generation "green" chemistry solutions being applied in hydraulic fracturing operations is a new complex nanofluid that replaces conventional surfactants, and is built around a completely natural and renewable citrus base. Based on nanoparticle engineering and using a food-grade orange oil termed d-limonene, the product is eminently sustainable, offers an extremely friendly environmental score card, and substantially improves post-stimulation well productivity.

In fact, the Green Check organization has approved the nanoparticle technology for stringent North Sea regulations for all ecotoxicology categories, including biodegradability, bioaccumulation, and aquatic toxicity to fish, crustaceans and algae. It contains no priority pollutants under the U.S. Clean Water Act, and there are no known or suspected carcinogens, halogens, ozone depleting chemicals, petroleum or benzene, toluene, ethylbenzene, or xylene products.

Field results of the new stimulation fluid have been nothing short of spectacular, and well productivity improvements have been documented in several basins. The nanotechnology illustrates the "win/win" potential of leveraging advanced frac fluid chemistry that improves environmental performance while improving production results.



One of the challenges in fracture stimulating both oil and gas formations in unconventional resource plays relates to fracture fluid recovery. Most of the slick water frac treatments pumped today in shale plays utilize very few chemicals. In fact, besides water and proppant, frac fluids typically consist of a biocide, a friction reducer and a surfactant in small volumes. By volume, the concentration of d-limonene-based complex nanofluid is typically very small, in the range of two gallons per 1,000 gallons of fluid pumped (0.2 percent). Other additives, such as biocides and friction reducers, often are included in even smaller concentrations.

## Fluid Recovery

In an ideal world, an operator would recover substantially all of the fluid pumped during a frac treatment so no water was left behind in either the formation or in the fractures created. High water saturation at the fracture face and within the propped fractures significantly impairs hydrocarbon flow into and through the propped fracture. Most wells stimulated in unconventional formations recover less than 50 percent of the original fracture water volumes, and frac load water recovery averages only 10-25 percent in ultralow-permeability reservoirs.

The unrecovered frac fluid remains trapped in the fractures and in the immediate region of the formation surrounding the induced fractures. This can have several detrimental effects, including reducing the relative permeability to hydrocarbons, creating a smaller effective

flow area, and leaving less effective fracture length, all of which lead to lower well productivity and recovery factors.

Through its nanoparticle complex, the d-limonene-based surfactant dramatically reduces surface tension and interfacial tension between the rock and injected fluids. The water is held in place by capillary forces that must be overcome in order for the gas or oil to enter and flow through the pack. This is exactly what this new green fluid does. It reduces capillary pressure, allowing more fracturing fluids to be recovered at lower pressures in an efficient piston-like manner. The reduced capillary pressure, in turn, allows better hydrocarbon entry into and through the created fractures.

In fact, the technology lowers capillary pressure and minimizes capillary end effects associated with well bores and fractures in low-permeability reservoirs by as much as 50 percent. In other words, it makes slick water even slicker and remediates formation damage. As a result of this more efficient dewatering, the fluid is also very effective in depleted or underpressured natural gas wells in both conventional and unconventional geologic settings.

In addition, the smaller proppant grains utilized in today's proppant packs have a stronger attraction to fluid, resulting in higher pressures necessary to dewater the pack. Moreover, it minimizes fluid adsorption on shales and fluid leak-off into the formation, both of which can lead to significant formation damage factors.

Increased water recovery (lower water

saturation inside and near the fractures) also means higher relative permeability within the fracture, which leads to longer effective fracture lengths for a given fracture volume. Additionally, effective fracture length deterioration caused by shut-in periods is less than half that of traditional surfactants used in hydraulic fracturing treatments, an important benefit to consider if wells must be shut in for any reason, including low natural gas prices.

## Improved Production

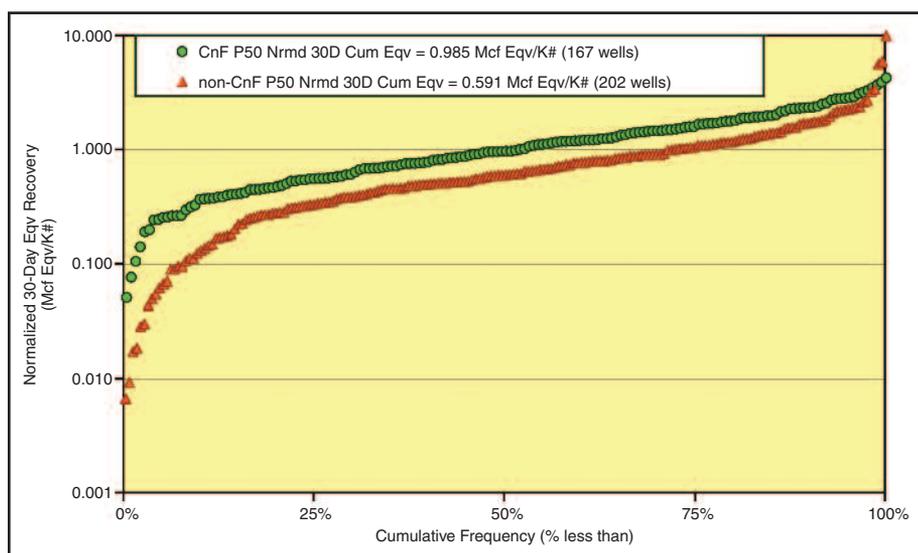
Improved production results have been obtained using this technology in many conventional and unconventional reservoirs and basins, in oil and gas wells stimulated in the Granite Wash, the Barnett Shale, the Signal Peak Field, the Fayetteville Shale, Appalachian Basin sands and shales (including the Marcellus and Utica shales), low-permeability sandstones in the Piceance and Uinta basins, the Vicksburg in South Texas, the Cotton Valley in East Texas, the Codell and Niobrara formations in the Denver-Julesburg Basin, the Green River Basin, and the Jonah and Pinedale anticlines as well as the Bakken formation in the Rocky Mountains, the Wolfberry in the Permian Basin and the Eagle Ford Shale. To date, more than 10,000 wells in 20 basins on six continents have benefited from the development and application of this nanotechnology.

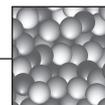
To assess the performance attributes of the d-limonene-based system, an independent analysis has been conducted to compare the results of several hundred wells in different environments pumped with and without the green surfactant.

Figure 1 shows a summation of all the public data sets in the five studies completed. Since the shortest production time was only 30 days, that became the comparative basis for this real-data production plot and no forecasting was involved. The cumulative frequency histogram shows the performance in terms of the gas equivalent based on fluid densities for 30 days, and is normalized for reservoir quality, pressure drawdown and treatment size.

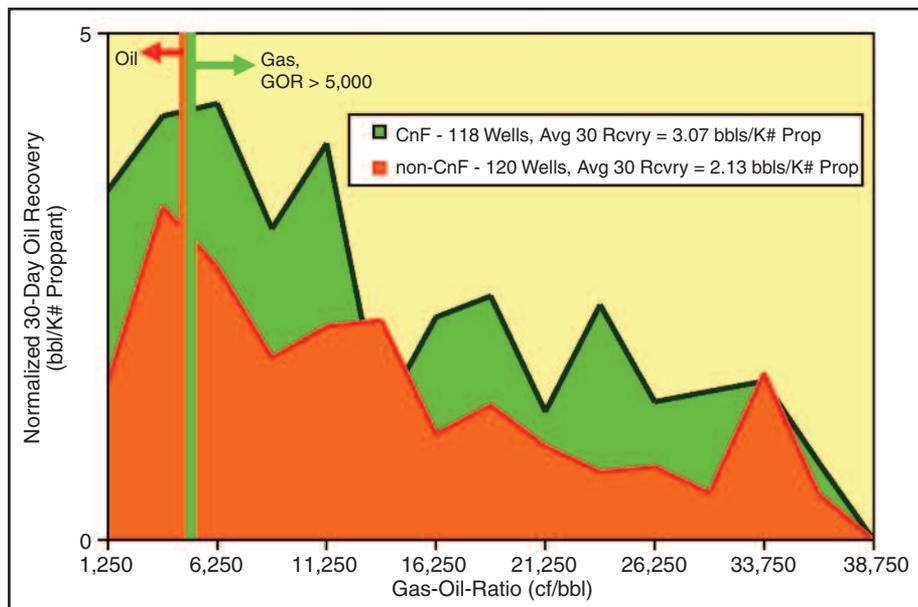
The 30-day equivalent recoveries are divided by the treatment size with respect to thousands of pounds of proppant placed. As can be seen, the observed normalized 30-day performance of the wells using the d-limonene-based technology was nearly 70 percent better than the wells using conventional surfactants. This well population includes both horizontal and vertical wells drilled in the Niobrara play

**FIGURE 1**  
**Normalized 30-Day Cumulative Equivalent Recovery**





**FIGURE 2**  
**Thirty-Day Oil Recovery versus Gas-to-Oil Ratio**



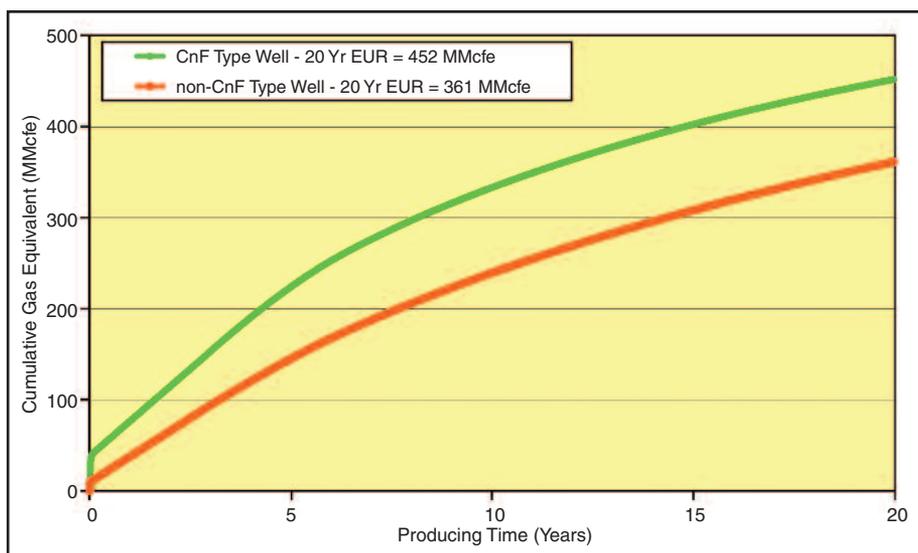
in the D-J Basin, the Lance formation in the Green River, and the Marcellus Shale in the Appalachian Basin.

Figure 2 is a comparison of the effect of using the technology in the two Niobrara well populations—"first fracs" and "re-fracs"—for a group of 118 wells using the d-limonene-based system compared with 120 wells without. As before, the populations were normalized for reservoir quality, drawdown, treatment size and limited to 30 days of observed production in order to include the newest wells. Longer production periods could have been employed, but that would have re-

quired forecasting production results for some of the wells.

The green values in the background of the figure represent 30-day oil and condensate recovery per 1,000 pounds of proppant placed in the 118 d-limonene wells, while the orange shaded area in the foreground denotes the 120 wells using other surfactants. As summarized in the box, the d-limonene wells recovered almost twice as much liquid hydrocarbons on average as the other group of wells in the first 30 days on production. Note that the graph also shows the traditional oil well/gas well gas-to-oil ratio cutoff of

**FIGURE 3**  
**Cumulative Gas Equivalent 20 Year Production Forecast**



5,000 cubic feet of gas per barrel of oil.

## Forecast Performance

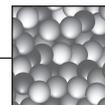
Finally, Figure 3 shows the projected 20-year forecast performance using type curves from a typical well treated with the d-limonene-based nanotechnology compared with a typical well treated with other types of surfactants. The figure incorporates the degradation in effective fracture length observed for both groups of wells. While the d-limonene wells can lose up to 25 percent of their effective fracture lengths in the first year, the wells without d-limonene can lose more than 50 percent, even though the actual performance for the latter group of wells is typically much lower.

The average permeability, thickness, porosity, drained area, etc., were the same for both "typical" well forecasts. The drawdown was also the same. The two well types were history matched to the observed, normalized long-term production



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Kevin Fisher is executive vice president of business development at Flotek Industries, and is involved in developing and marketing green fluid chemistries to optimize the hydraulic fracturing process. He began his career with Halliburton in 1979 and served for 14 years as logging engineer, field supervisor, log analyst, U.S. sales manager, and global technical marketing manager. Fisher joined Pro-Technics as director of sales and marketing in 1993 and Pinnacle in 2000, eventually serving as chief executive officer until Pinnacle was sold to Halliburton in 2008. Fisher then served as general manager of Pinnacle, a Halliburton Service, until he joined Flotek in 2011. He holds three U.S. patents related to spectral gamma ray, gravel pack density logging, and tiltmeter instrumentation. Fisher holds a B.S. in natural science/physics from Cameron University.



performance for both the d-limonene and “other surfactant” well populations by adjusting the effective fracture lengths for each. The daily rates then were summed to generate the cumulative production curves over 20 years. The gas-to-oil ratio for the equivalency was based on the data in Figure 2.

In both cases, the cumulative curves start steeply upward, and then flatten to their longer-term performance slope. That arises because of the predegradation fracture lengths, allowing higher production rates. The forecast production curves for

the wells using conventional surfactants break over earlier, and at lower cumulative production, because of the earlier onset of more severe fracture length degradation.

As these real-world field data demonstrate, it is imminently possible to both improve the environmental attributes of frac fluids and optimize production results. Frac fluids are recovered more completely and in less time, leading to oil or gas to the sales line more quickly as well as higher initial productivities and better ultimate recoveries. Poor wells produce

better and good wells produce great. The improved well performance, coupled with the advantages of pumping a green fluid chemistry, create compelling operational economic justifications for continuing to develop and deploy next-generation frac fluid chemistries. □

**Editor’s Note:** The author would like to thank Dr. Jim Crafton of Performance Sciences Inc. for his work in normalizing and comparing field results in the study areas.