BIODIESEL MAGAZINE

The Many Faces of Distillation

The best path depends on the individual plant and who you ask

By Ron Kotrba | March 12, 2013




Since 2004, there have been 15 modifications to ASTM D6751, the biodiesel quality specification, according to Teresa Alleman, senior chemist at National Renewable Energy Labs in Golden, Colo., providing evidence for the assertion that the biodiesel quality spec is ever-tightening. The latest iteration in the evolution of D6751 is the passage of the voluntary No.1-B grade of biodiesel, establishing the first-ever monoglyceride limit at 0.4 percent and mandating a 200-second, year-round cold soak filtration test time limit. Some in the industry suggest that the only way many producers will be able to manufacture a fuel that meets these new targets, in addition to any future improvements to the quality spec, is through employing distillation on the backend of the production process—particularly if low-cost, low-quality feedstocks are utilized. “The American Petroleum Institute is pushing for tighter and tighter specs on biodiesel, therefore, making producers have to put in additional equipment,” says Ernie DeMartino, president and CEO of Pearland, Texas-based Biodiesel Experts International. “And the margins are so tight already, what they want to do is push them out of business.”

It’s not only the ASTM standards that are increasingly tightening. Customer purchase requirements also dictate end-product fuel quality and, indirectly, process changes or upgrades. For instance, there is no color spec in D6751, so what does it matter if distillation produces a “water-white” biodiesel? “The color spec is dictated by the customer,” DeMartino says. “Just like there are customers that will only buy biodiesel made from soy, there are customers that will only buy water-white biodiesel.”

Brian Mattingly, general manager for Washakie Renewable Energy, a 10 MMgy biodiesel production facility with distillation capabilities in Plymouth, Utah, says, “From a market standpoint, a lighter-colored fuel is nice for customers to be able to see. Generally, the color of your feedstock does impart some color onto the finished fuel, so if you’re starting with a very dark feedstock, you’re not necessarily going to end up with a water-white fuel, but distillation does cause a marked improvement in the color of the fuel.”

As the industry has progressed, refined soybean and other virgin vegetable oils have gotten too expensive for many producers to use and remain profitable, except for those with captive stocks. “People have moved more toward lower-quality but more economical oils, such as rendered oils, animal fats and used cooking oils, which tend to be higher in free fatty acids and darker in color,” says Kirk Cobb, senior process design engineer with Superior Process Technologies Inc., a subsidiary of Baker Commodities. “After the fuel is produced it’s oftentimes absolutely black—it looks like coffee. It might be in spec, but marketing a really dark, undistilled biodiesel may be a real challenge.”

Another reason for the move to distillation is the continued tightening of ASTM specifications to lower light metals content and the ability to remove sulfur to comply with the ultra-low sulfur diesel regulations, says Doug Smith, R&D and quality assurance director at Baker Commodities. “Whether the biodiesel is not in spec due to incomplete reaction or contaminants from lower grade feedstocks, distillation is a proven way of bringing that biodiesel back within specifications in one process unit operation,” Smith says.

Mike Powers, an engineer with Pfaudler Inc., says, “In general, with the current ASTM biodiesel spec, you can have, in my opinion, a very poor-quality fuel and still meet those specifications.” He believes that the spec will, and must, continue to evolve. “At some point distillation will be, certainly for the lower-priced feedstocks, a requirement,” he says. “I can’t come up with a process that wouldn’t benefit from it. It does not cure all of the potential problems in terms of other contaminants—some of the components are actually difficult to separate with distillation—so your chemistry needs to be working up front of distillation to begin with.”

There is not one right answer to what distillation setup a producer should use, or if they even need to distill at all. Derek Masterson, product sales manager with Minneapolis-based Crown Iron Works, says while CIW is happy to provide any size and variety of distillation system tailored for a customers’ specific needs, it’s a highly energy-intensive process, “which is why we don’t recommend it as a first choice,” he says. Masterson says for producers seeking to improve the quality of their fuel, they should fully investigate whether adding an additional reaction step in-process might get them where they want to be, before making the decision to install distillation equipment. “If they can tweak the pretreatment or transesterification reaction and get a better product than what they have now, maybe distillation isn’t necessary,” he says. “Those kinds of things have to be thought about. We sell the equipment, and it’s by far the most expensive equipment to buy and run compared to other pretreatment and things you could possibly do, so it needs to be shown to be necessary.”

Distillation is not just a simple unit operation, says Cobb. “There are many different options and process parameters to consider: there are distillation towers with reboilers, wiped film evaporators, vacuum distillation, atmospheric distillation, steam-heated, hot-oil heated, single-stage flash units and multistage fractionation columns,” he says. “If you’re distilling methanol there’s steam-heated with no vacuum, but many stages of fractionation may be required. In contrast, distilling methyl esters will require thermal oil heating under vacuum, but little or no fractionation. It takes someone who’s familiar with all of these variations to put a plant design philosophy together.”

Mattingly says B100 distillation is set up to be the very final step in WRE's process. "We do two stages of reaction, then settling after each, then we go through ion exchange resin and then we demethylate, and after that we go into day tanks so we can check the overall quality of our fuel," he says. "And it is at that point when we decide if we need to distill our product."

In a biodiesel facility there are three potential streams to distill or evaporate—methanol (wet or dry), biodiesel and glycerin—and each of these materials typically requires a different set of operating conditions. Cobb says if you have wet methanol from water washing, a fractionating column is needed with a lot of dry methanol reflux going in at the top of the column to strip out the wash water at the bottom of the tower. "That's all done at fairly low temperatures because the methanol comes off the top of the column at 148 degrees Farenheit, and the water going out the bottom is basically boiling water, 220 degrees," Cobb says. "That's an atmospheric column, steam-heated, but it uses a lot of energy due to all the reflux needed to dry the methanol, and methanol has a relatively high heat of vaporization (475 to 500 Btu/lb, depending on conditions). In my opinion, when you design a plant, you can go the traditional route with water wash and methanol recovery, or you can avoid water washing, strip dry methanol out of the biodiesel first, with little or no reflux required, and then distill the biodiesel under vacuum conditions using a thermal oil heating system. Overall, this approach will use a lot less process energy, and results in higher quality product."

Masterson says imagine a cup of layered liquid with the top being the lightest, followed by the middle product, with the heaviest layer at the bottom. You can put three straws in to remove the different stages of liquid, which would represent a more sophisticated, expensive fractionating column, "but it's sure a heck of a lot easier not to do it that way," he says. "So removing the methanol is always step one." It's surely a lot easier to wash the fuel at low temperatures and atmospheric pressure followed by demethylation then distillation rather than pushing everything through distillation. If that were done, Masterson says, "now you'd have exactly the same thing, with no monoglycerides, so you'd have to figure out how to strip them one at a time, the more volatile first, or you'd have to design a distillation column that's a lot more complicated to take off the top, middle and bottom."

Biodiesel distillation is a different animal than stripping methanol, Cobb says. "Once the methyl esters have been stripped of any methanol or water and you want to distill the biodiesel, that is done under vacuum at 2 to 3 millimeters Hg (mercury), so you're under vacuum and approaching 400 degrees," he says. "Methyl esters have a heat of vaporization of only 125 to 130 Btu/lb so distilling biodiesel uses less energy than recovering dry methanol from wet methanol. But you have to do it under vacuum." For classical biodiesel distillation column, there's no fractionation involved. Product is pushed through the reboiler and everything that is volatile evaporates; there is typically structured packing above the reboiler vapor inlet so the pitchy materials on the bottom cannot be carried out the top of the column into the distilled methyl esters. But this can't be done with typical 150-psig steam, which will only produce temperatures of 360 degrees at most. To distill biodiesel, high temperatures are needed. Thus, a hot oil heater system (typically operating at 500 degrees) is required, which must be included for projects, or added to existing plants thinking about installing biodiesel distillation.

"With classical distillation there in an inherent pressure drop associated with moving the vapors through the column," Powers says. "The wiped film evaporator basically eliminates this pressure drop because the vapors travel radially inward a very short distance before collapsing on the internal condenser. All of the liquid within the wiped film evaporator is exposed to the deep vacuum level so the operating temperature is minimized. The rotating entrainment separator between the heat transfer surface and the internal condenser allows us to operate with a high heat flux while maintaining distillate purity so, with a relatively small evaporator, we can drive a high throughput. The space requirements for a wiped film evaporator system will be less than a classical distillation system. The capital cost may be slightly higher for the wiped film evaporator system but the energy cost will be less and the recovery will be higher."

Cobb says it's not inconceivable to use a wiped film evaporator for distilling biodiesel, "but that's your high-volume material and wiped film evaporators get pretty expensive," he says, adding that it may be more economical to use a standard distillation tower for biodiesel. Nevertheless, depending on the feed oil quality, both options are worthy of consideration. However, if there are any residual monos in the crude methyl esters, they may distill out with the product stream from a wiped film evaporator. In contrast, using a conventional column with a bit of structured packing and a bit of reflux, monoglycerides can then be removed with a small bottoms cut.

"Some folks considering biodiesel distillation may be concerned about yield loss associated with the distillate bottoms produced," Cobb says. "But, the distillate bottoms may actually generate less yield loss than those associated with water washing, and the resulting soap formation and emulsions they create." Masterson asks, "What do you do with the stuff you have left over? It doesn't disappear. Let's say you have a yield of 95 percent of better biodiesel and you have 5 percent left over, it's probably mostly methyl ester, probably saturated methyl esters, maybe some C18s, monos, what do you do with that? It's burnable, it has Btu value, there's no doubt about that because it was already biodiesel anyway, it probably would have been an acceptable product, so if your biodiesel process was so bad that you're pushing all your problems to the end, I don't know what you're going to do with that material." Powers adds that plants seeking to expand and already have classical distillation columns may minimize their yield loss by installing a wiped film evaporator in series to take the concentrated bottoms from the distillation column and run it through the wiped film evaporator to maximize sellable product.

For plants already outfitted with biodiesel distillation that are seeking to expand production rates, the vapor loads, reboiler and condenser heat duties for the column must be evaluated. "If you have an existing distillation tower that's designed for a certain capacity with a certain vapor load, you simply can't go beyond that vapor load or you could start entraining the nonvolatile pitchy materials (color bodies, dimers, polymers, and other heavy boilers) that you are trying to take out," Cobb says. "Vapor density and vapor velocity must all be considered when calculating what's called the 'F-factor', or flooding factor, and depending on the type of structured packing used in the column, this dictates the range of F-factors in which the column design can operate." He adds that if someone were batch distilling, and they wanted more capacity, they could switch to continuous distillation and get more annual capacity out of an existing column.

The glycerin byproduct can also be distilled to significantly increase its market value. The glycerin stream is typically less than 10 percent of the volume of the biodiesel, but it may also contain the most impurities. "First, the methoxide catalyst, which is very soluble in glycerin, must be neutralized with acid," Cobb says. "This forms inorganic salts. After stripping methanol from the glycerin, the crude glycerin can be vacuum distilled, but due to the presence of salts and other nonvolatile solids, such as soaps, glycerin is typically distilled in a wiped film evaporator. The glycerin will distill out the top of a wiped film evaporator and the salts and other solids will drop out the bottom. A wiped film evaporator has a rotating device inside that constantly wipes the solids off the heat transfer surface to keep it clean, and drives the solid materials out the bottom; the glycerin bottoms may typically be 20 percent of the feed, and the distilled glycerin may amount to an 80 percent yield." Glycerin distillation would also be under vacuum, not quite as deep as biodiesel distillation, perhaps 5 to 10 mm Hg rather than 2 mm Hg for the biodiesel, Cobb says.

"Glycerin is the dirtiest of the crude streams," Powers says. "It's got all of the salts and soaps and chemicals. There are those who run glycerin through distillation columns, but I can only assume that they have all kinds of maintenance issues with putting something so cruddy into a distillation column." Powers says there are three stages in a biodiesel plant where wiped film evaporators are suited to perform: on the frontend for stripping of free fatty acids, biodiesel distillation, and glycerin distillation.

Artisan Industries has a piece of equipment called the Rototherm V, which the company says can distill biodiesel and glycerin at the same time. The equipment can also be used in an initial stage prior to distillation to remove the methanol. "[Rototherm] recovers 99.9 percent of the solvent for recycl[ing] back to the reactor," Artisan Industries' website states. Biodiesel Magazine reached out to engineers at Artisan Industries for information, but did not receive a response. "If necessary, the solvent and water removed in this step can be vapor-fed directly to a distillation column to purify and dehydrate the solvent. In the second step, a Rototherm is operated at low absolute pressure to vaporize the glycerol and methyl esters plus any remaining traces of light ends. The vapor from the Rototherm flows out through a vapor/liquid separator to knock back any entrained liquid and enters a special, large void-space, low-pressure drop condenser using tower water as coolant, where the methyl esters and glycerin condense. The residual solvent and water vapor flow through a direct contact (barometric) condenser to a shared vacuum system, which uses sprays of cool recirculating methyl esters to minimize the loss of [methyl esters] and glycerin to the vacuum system. The condensed methyl esters and glycerin flow to further processing downstream to separate the phases and remove any remaining free glycerin from the fuel." While many agree this is a novel approach, some express concern that distilling the biodiesel and glycerin together may lead to a reverse reaction in which glycerides and methanol are formed from the glycerin and methyl esters.

Ultimately, like many stages in biodiesel production, most experts say there's no wrong answer in how to go about employing distillation at a biodiesel plant. "I can tell you which way is more economical than other ways," Masterson says, "but it could be the wrong answer for a specific plant because of the fats or quality of materials used. So we, Crown Iron Works, and other vendors like us are happy to tailor the plant for the customer. We don't have off-the-shelf distillation plants that we say, 'use this and everything will be fine.' I don't think that's the right way for the biodiesel industry in any step, whether it's pretreatment, transesterification or distillation."

In the end, pinpointing a timeline for return on investment may not be so easy for a biodiesel plant looking to install distillation capacity. "Now that there's a second grade of biodiesel, there may be an answer for that," says Masterson, who adds that the price differential between No.1-B and No.2-B probably would not be incentive alone to purchase and operate distillation. "If you need to use lower-cost feedstocks to survive, however, then I don't think it's a return-on-investment question, it's a stay-in-business question."

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