Salvaging potentially reusable methanol is a vital step in keeping costs down, but when and how this is achieved is still up for debate

Removing the excess

Methanol extraction and recovery during the manufacturing of biodiesel is a crucial step in the successful and profitable operation of a biodiesel plant. The most important reason is to meet ASTM D6751 or EN14214 specifications. To meet these requirements, the flash point must be above 93oC, and the methanol content must be below 0.2v%. The second reason for recovering methanol is cost efficiency. Methanol is a major cost in the production budget, so not recovering this potentially reusable ingredient limits the ability to be profitable. For these reasons, careful consideration needs to be given to when and how the methanol is removed from the process.

During both the pre-treatment esterification and the production transesterification steps, methanol is reacted in the presence of a catalyst to make methyl-ester (biodiesel) based on the stoichiometric ratio for this reaction. However, to maximize the reaction efficiency, an excess, or more than the stoichiometric requirement, of methanol is added to help force the reaction to completion. Depending upon which feedstock and catalyst being used, the excess methanol will need to be removed in one of two locations during the process. It will either be mixed with water from the reaction of the free fatty acids in the esterification step, or will be distributed between the methyl-ester and glycerin produced during

Methanol Recovery from 100 gpm biodiesel

transesterification. The details of methanol removal in the both the esterification and transesterification steps are shown below.

In the esterification step, the primary objective is to extract the water generated during the reaction before further processing the product stream into methyl-ester. However, in removing the water, the methanol will also be removed. This extraction can be accomplished with either a distillation column, or a less complicated flash extraction tower. In either case, the resulting methanol/water stream needs to be further processed to dehydrate the methanol before reuse. Methanol dehydration is commonly performed by distillation column. However, a lower energy alternative is dehydration by a molecular sieve dehydration unit (MSDU).

In the transesterification step, methyl-ester is produced along with an additional 10wt% glycerin in an excess of methanol. The methyl-ester is then separated from the glycerin using a centrifuge or by allowing the two phases to separate by decanting. When this separation occurs, the excess methanol is distributed between the two steams with a higher affinity for the glycerin than the methyl-ester. Generally 60% of the excess methanol removed stays in the glycerin stream. A detailed breakdown of methanol removal from the resulting streams is found below.

- Methyl Ester: This stream will normally have 3-10wt% methanol in it. The objective of the methanol extraction for the methyl ester phase is to reduce the methanol levels to meet ASTM or EN specifications. This is commonly accomplished in one of two ways:

1) Water wash: If using a water wash, water is trickled through the methyl ester to remove any methanol and other impurities. However, this method then necessitates that the water is removed from the biodiesel in a biodiesel dehydration step. In this case, the removed methanol is diluted with a large amount of water.
2) Flash extraction tower: If a dry wash resin is being used, then the excess methanol can be removed to meet ASTM/ EN requirements with a properly designed flash extraction tower. If the process recipe had no water at this stage, then the recovered methanol can be reused directly.

- Glycerin: The objective of the methanol extraction for the glycerin phase (typically 20-60% methanol) is to reduce the hazard level of the glycerin for transport or sale, and to recover the methanol for re-use, thus reducing your costs. This extraction can be accomplished either using a distillation column or flash extraction column.

Technology considerations

Methanol has a relatively high vapour pressure (low boiling point), so it vapourises fairly easily in pure form. However, when extracting methanol from a mixture down to the very low residual levels required, the process is much more difficult in design and in practice.

As many biodiesel producers have found, a simple flash pot may not remove enough methanol to satisfy the ASTM or EN requirements. It is generally advisable to use distillation columns or flash extraction towers (FETs) to achieve this. Both distillation columns and FETs are designed with the help of modeling software such as ASPEN or ChemCad which can easily take into account the complex vapour-liquid equilibrium calculations necessary to accurately describe the separation process. While both of these options add cost, they are invaluable units which can ensure that theend product will meet the applicable requirements.

The degree of automation necessary should also be reviewed. A fully automated design is often the easiest to operate, but there is usually a significant cost associated with this. A different, lower cost option is a semi-automated unit that would require only intermittent operator attention for continuous operation. There are some equipment designs discussed that require full automation, such as distillation columns and continuously operating molecular sieves; while flash extraction towers are offered in both semi- and fully-automated configurations.

When working with outside engineers or equipment manufacturers it is important to carefullyspecify the process requirements. The specified requirements for the extraction equipment, such as starting concentration and required final purity levels, directly affect the equipment design, capital cost, and energy required. It is prudent to include a safety factor, but the safety factor can have an unintended effect on the design if it is not handled properly. For example, assume there is a mixture of 5% water in 95% methanol and the purity required is 99.5% MeOH/ 0.5% water. Specifying the starting level at 6% water/94% methanol would be appropriate to give some safety without greatly affecting the equipment cost; however, revising the final concentration at 0.05% water can greatly affect the distillation column height or energy (reflux and boil-up ratios).

Distillation columns are commonly used for the liquid-liquid extractions and recovery steps, including biodiesel-methanol, glycerin-methanol, and methanol-water. For any specific process requirement there is a cost trade-off between the initial cost (number of stages, overall height, etc) versus operating cost (reflux ratio, boil-up ratio). Typically, purity requirement is set on both the top (i.e. methanol) and bottom (glycerin, biodiesel or water) products streams of the tower. Very high purities can be achieved using a distillation column. This equipment is quite sophisticated, requires full automation, and thus can be quite expensive. Even with full automation, these columns require a thorough understanding of its operation and troubleshooting by the operators. Heights can be in excess of 40 feet, limiting location at some sites.

Flash extraction towers (FET) are also commonly used in biodiesel-methanol, glycerin-methanol, feed-oil-water, and biodiesel-water separations. Although more limited than distillation columns, these units are simpler in design and operation. FETs are not however the same as a flash pot. While a flash pot is simply an empty pot in which a liquid steam is flashed in a single unit operation, a FET is a multi-unit operation, where the flash is only one method of separation included in the design.

Once designed for a specific set of requirements, this equipment can handle any less stringent variation without the need to change process parameters. Being less complicated, this design is easily understood by operators and requires little attention once operating. This design is available in semi-automated or fully-automated designs. Newer units can come skid mounted, fully pre-piped, pre-wired with heights below 12' so units can be shipped complete, with minimal on-site hookups.

Methanol Recovery from 7 gpm glycerin

Molecular sieve dehydration units (MSDU) for alcohol-water (methanol, ethanol, IPA, etc) separation are typically limited to water concentrations less than 10%, although these can be designed up to 20% water. To date they are not common in biodiesel production because of the small flow demand in biodiesel production compared to other applications. However, molecular sieves have been in existence for 40 years and have become the standard method of dehydration in natural gas and ethanol processing. Molecular sieves use adsorption to perform separations much like activated carbon beds. However, the sieve material is made specifically so that they can selectively adsorb water while excluding the larger alcohol molecules. These units are offered in fully automated designs only. A key advantage of this design is much lower energy, up to 30-60% less energy than distillation. Units up to 25 gpm can come skid mounted, fully pre-piped, pre-wired with heights below 12' so units can be shipped complete, with minimal on-site hookups.

Future outlook

Methanol extraction is a necessary step in the successful production of biodiesel, and is required in several steps of the process. No matter at which stage the methanol is removed it is important to review the available options and ensure that the equipment used is effective and will produce a product that meets specification.

For more information:
This article was written by Paul M Winter, president of Wintek Corporation, paul@wintek-corp.com, www.wintek-corp.com