Improper handling of methanol has been the result of many accidents, hampering the safety record of the biodiesel industry

Playing it safe

Methanol is the typical alcohol of choice for reacting with fats and oils to produce biodiesel and glycerine, although ethanol and isopropanol are acceptable too.

Since 2006 to the end of 2009 there have been approximately 20 explosions and/or fires in biodiesel plants in the US alone with the majority resulting from the mishandling of methanol. There have been 2 fatalities in the US associated with the above accidents.

Methanol has a very wide flammable envelope at ambient temperature and an even wider envelope at 65°C, a typical biodiesel reaction temperature.

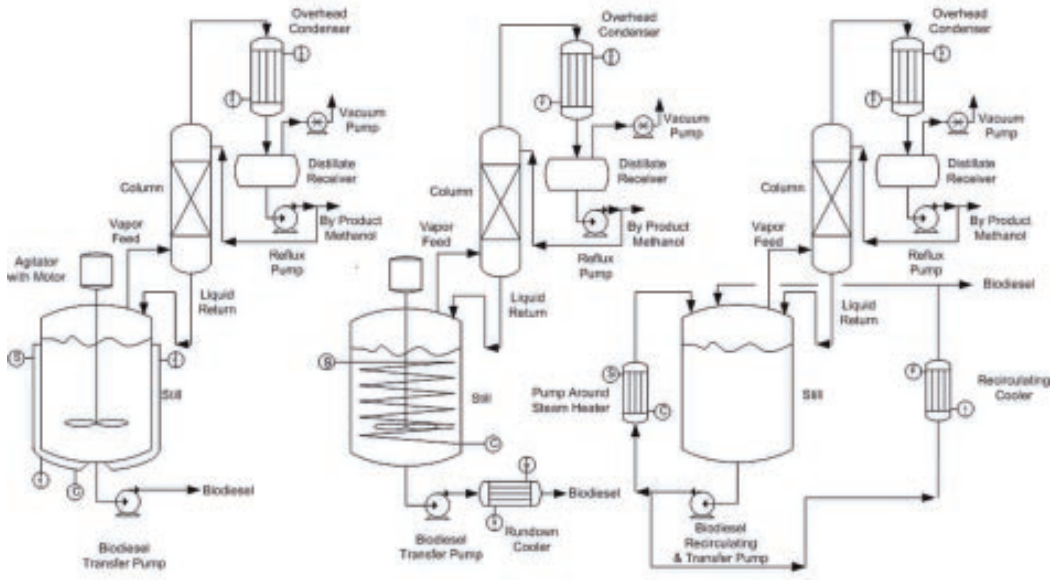
Thus the usage and recovery of excess methanol is important from a safety standpoint and an economic standpoint since the recovered methanol can be reused at the front end of the plant.

Typically double the stoichiometric amount of methanol is used in the biodiesel reaction to drive it to the right that is towards biodiesel and glycerin.

This excess methanol partitions with some going into the biodiesel phase and some going into the glycerinephase in the phase separator(s). On a weight basis more goes into the glycerine phase. At this point there are typically two ways to process biodiesel: the water wash method or the dry wash method.

In the water wash method the biodiesel is passed through an extraction column or process that provides intimate contact between the biodiesel and a purified water phase. The methanol and sodium soaps in the biodiesel move into the aqueous phase. The soaps are a by-product from the sodium metholate catalyst reacting with free fatty acids in the original feedstocks.

Batch distillation unit with three ways of heating and cooling



The water/ methanol stream goes to a continuous distillation system to remove the methanol from the water stream. In a smaller plant this could be a batch distillation system.

The current trend is to go to a waterless biodiesel process such as the dry wash process supported by Lanxess and Dow Chemical. In addition the newer solid catalysed or enzyme catalysed esterification/ transesterification dual process do not use water either.

Distillation

Distillation is an integral part of any biodiesel plant. It allows producers to recycle the excess methanol used in the transesterification reaction back to the front end of the plant. This is a major cost saving and also allows companies to meet the ASTM D93 Pensky Marten closed cup flashpoint test, which requires a reading of 130°C or greater.

This simply indicates that enough methanol has been removed from the biodiesel to meet the flammability specification. Water washing can also achieve this but this results in a water/ methanol stream that must be further processed. The water stream will in fact contain other impurities including monoglycerides, diglycerides and soap. Pretreatment and post treatment are not covered in this article. First we will review a few key concepts in distillation.

Reflux

Reflux refers to the portion of the condensed overhead liquid product from a distillation column that is returned to the upper part of the column. Inside the tower, reflux liquid provides cooling and condensation of the up flowing vapours, thereby increasing the efficacy or efficiency of the distillation tower. The more reflux provided, the better is the column's separation of lower boiling materials from higher boiling materials. However energy costs are dramatically increased as reflux is increased since the returned or refluxed liquid must be boiled up again from the still. To use less reflux a taller column is required to obtain the same degree of separation. There is always a trade-off of operating costs versus installed costs. A taller more expensive column has lower energy costs and a shorter less expensive column has higher energy costs. This applies to both batch and continuous distillation.

Vacuum

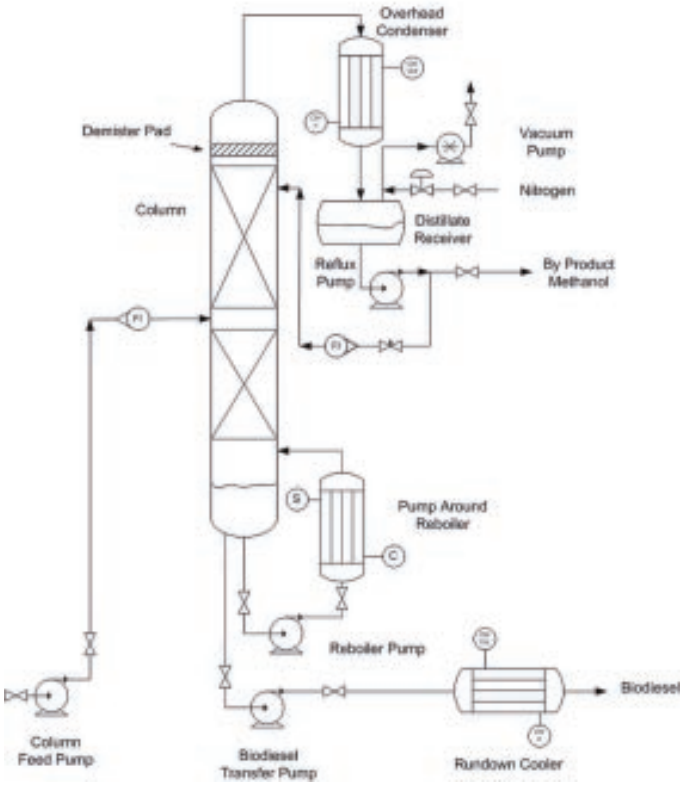
Vacuum lowers the boiling point of methanol and for that matter all chemical compounds. In addition this keeps the biodiesel far below the thermal degradation point.

Batch versus continuous

Depending on the size of the plant two options are available: batch or continuous distillation.

Continuous distillation is usually less capital intensive but requires round the clock operation. Continuous distillation also does

Continuous distillation unit



not like to be started up and shutdown. The unsteady state conditions that occur may cause off spec product to be produced. On startup a continuous column may not produce on spec product until the column lines out (reaches steady state).

All column variables including temperatures, pressures, liquid levels and flowrates are steady and not fluctuating. Batch distillation is very forgiving. If the methanol content in the still is too high at the end of a batch (low on flash point) then you simply run the still again to remove the residual methanol. Continuous on the other hand could produce off spec biodiesel (high methanol content) for minutes or hours until someone performs a flashpoint test. Off spec. biodiesel must be rerun through a rerun tank to get it back to the continuous distillation column.

Typically batch distillation is coupled with batch reactors and continuous distillation is coupled with continuous reactors.

Continuous distillation

The biodiesel continuous distillation system consists of a trayed distillation column with certain stages of distillation. The biodiesel/ soap/ methanol mixture is fed to a midpoint in the column, recovered methanol comes off the top of the column and methanol free biodiesel comes off the bottom. A shell and tube heat exchanger serves as the overhead condenser and condensed liquid flows to a distillate receiver. Recovered methanol flows from the distillate receiver on a level control system consisting of a level indicating controller located within the PLC, a level transmitter located on the distillate receiver and a variable speed pump that pumps to the methanol storage tank for recycling and reuse.

A separate pump sends recovered methanol back to the top of the column as reflux. The reflux rate is set by a flow indicating controller (FIC) located within the PLC. The associated flow transmitter is located on the discharge of the reflux pump and the output of the FIC controls the variable speed drive on the reflux pump. The bottom of the column consists of a kettle type reboiler with a level controller on the reboiler that pumps down the finished biodiesel to the storage tank. The biodiesel at this point still contains a bit of soap if sodium metholate was the catalyst and this soap can be removed with one of the ion exchange resins where the soaps and any unreacted monoglycerides or diglycerides adhere to the surface of the beads or even a magnesium silicate material to remove these materials. Once the biodiesel reaches the bulk storage tank an antioxidant will be added to the finished material. With dual esterification/ transesterification processes no soap is present so these distillations of methanol and biodiesel are even simpler.

Batch

Batch distillation is time dependent and requires preparation of time cycles on a Gant chart so that each task can be estimated in minutes and the overall cycle time to distill off the methanol can be calculated. Typical tasks on the Gant chart include pumping time to charge the batch distillation unit (still), heating up the batch, distilling off the methanol, cooling down the batch and pumping time to empty the still. Other things that tie into the Gant chart are: how long does it take to complete a batch of biodiesel and glycerol in the batch reactor? How long does it take to settle out the glycerol in holding tank? Is the company using a centrifuge while pumping from the batch reactor to the holding tank? As soon as the still is empty another batch of phase separated biodiesel in the holding tank that is ready to be charged into the still.

The batch still is charged with biodiesel and methanol after the glycerol has phase separated by settling for by centrifuge. The vacuum pump turned on. The vacuum is drawn down to the desired vacuum and the steam on the jacket is turned on. During the initial boil up phase of methanol vapor all that is condensed by the overhead condenser is returned to the distillation column and will not be drawn often as methanol byproduct. This is called total reflux mode. Of course there must be a liquid level in the distillate receiver in order to start the reflux pump. At this point the column should be at steady state conditions. With a specific rate set on the reflux pump the methanol should be removed from the distillate receiver on an automatic or manual level control system. Some distillation systems require that the reflux rate change over the cycle time of the distillation unit. When the entire methanol has been distilled off of the biodiesel, the steam is turned off to the still, the vacuum pump is turned off and nitrogen gas is allowed to flow backwards into the still instead of air. The nitrogen gas is strictly a safety precaution and prevents the buildup of a methanol/ air explosive mixture inside the still. At this point the biodiesel is pumped down from the still through the run down cooler and on to post treatment and final storage.

In the batch distillation process there is the heat up phase and the cool down phase with the purification by distillation occurring in between. Heating up the batch can be performed by a steam jacket on the distillation pot, an internal coil or a pump around shell and tube heat exchanger. Likewise cooling of the batch can occur by one of the same three methods

For the dry wash method any unreacted monoglycerides or diglycerides, soap and biodiesel goes to either an ion exchange resin or a magnesium silicate.

A type of system not recommended is an air stripping column to remove methanol from biodiesel. This system is a bomb waiting to happen. In this system biodiesel/ methanol and soap pass down a packed column and air is up through the column with a vacuum pump. The air does successfully strip the methanol out of the biodiesel however the air methanol mixture can be inside the flammable envelope. If an ignition source is present an explosion and fire may result. ●

For more information:
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