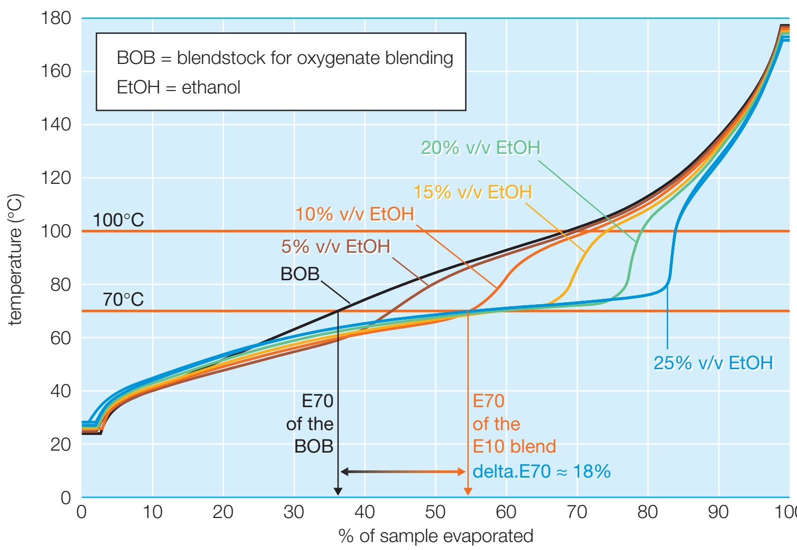
Understanding the volatility of ethanol/gasoline blends

A laboratory study probes complex blending behaviour by observing the impact of ethanol content on the distillation properties of gasoline blends.

The EU's Renewable Energy Directive (RED, 2009/28/EC) mandates that 10% of transport fuels on an energy basis must be derived from sustainably produced, renewable sources by 2020. As also required by the RED, each Member State must evaluate how they intend to reach their individual mandate based on their unique combination of energy resources and transport demands. The results of these evaluations have been published in each country's National Renewable Energy Action Plan (NREAP). In general, the NREAPs anticipate that conventional bio-components, such as ethanol from sugar fermentation and fatty acid methyl esters (FAME) esterified from natural oils, will largely be used to meet the 2020 mandates because of the slower pace of development of more advanced bio-components. Although today's EU-wide specifications allow up to 5% v/v ethanol in gasoline (E5) and up to 7% v/v FAME in diesel fuel (B7), work is progressing in the European Committee for Standardization (CEN) to increase these blending limits.

Both ethanol and ethers, such as ethyl tertiary-butyl ether (ETBE) or methyl tertiary-butyl ether (MTBE) will be used to increase the oxygenate fraction in gasoline fuels. Because of its special properties, however, ethanol imparts especially large property changes when it is blended at low concentrations into gasoline. An example of the effect of ethanol on gasoline's distillation curve is shown in Figure 1.

Figure 1 Effect of increasing ethanol content on the distillation curve of an ethanol/gasoline blend



The % evaporated at 70°C (E70) and at 100°C (E100) are two important specification parameters for gasoline because these values are known to have an effect on the driveability performance and emissions of gasoline-fuelled vehicles. When gasoline is specifically manufactured for blending with oxygenates, it is usually called a 'blendstock for oxygenate blending' or BOB.

Increasing the amount of ethanol in gasoline changes the distillation curve of the blend, substantially increasing the E70 distillation point as shown in Figure 1. This effect is larger at 70°C than it is at other distillation temperatures because the boiling point of ethanol is very close to this temperature. In order to ensure that the E70 of the ethanol/gasoline blend remains below the maximum specification value allowed for market fuels, the volatility of the BOB must be lowered by adjusting the composition of the BOB. This has an impact on refinery production because the molecules removed from the BOB to accommodate the ethanol must find a home in another petroleum or chemical product.

CONCAWE evaluated the published literature associated with this effect, as well as the impact of volatility changes on vehicle performance (see CONCAWE Report 8/09). The results of this review showed that the analytical data on different ethanol/gasoline blends are limited, especially for ethanol concentrations at 10% v/v and higher. The lack of enough reliable data and predictive models for the effect of ethanol on the blend's volatility makes it difficult to anticipate what properties should be controlled to ensure that ethanol/gasoline blends are always on-specification and cost-effectively manufactured.

To develop these data and explore these effects, CONCAWE and Shell Global Solutions UK formed a consortium in 2009–2010. This project was called the 'Bioethanol/Petrol: 5-25 Study' or BEP525 and was supported by the European Commission. The objectives of the study were straightforward: to vary the composition and properties of the gasoline BOB over a wide range allowed by the CEN EN228 gasoline specification, and quantitatively measure the effect of different ethanol concentrations on the distillation curve of the blend.

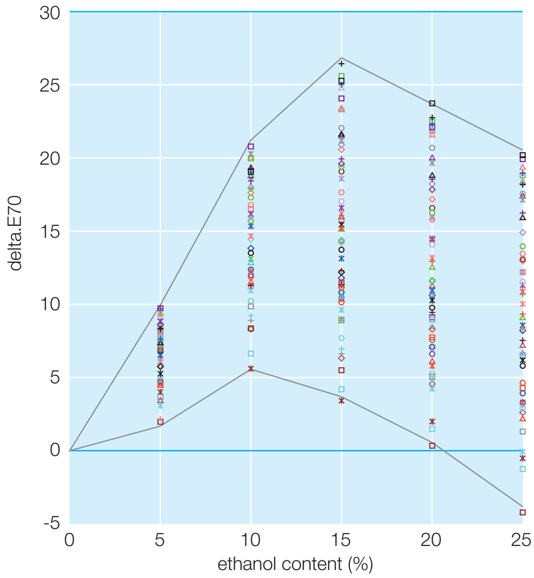
For this study, 60 different gasoline BOBs were blended from typical refinery streams spanning a wide range in hydrocarbon composition and initial volatility. Five different ethanol/gasoline blends, from 5 to 25% v/v ethanol, were made from each BOB, and the properties of the resulting blends were re-measured using a variety of analytical techniques. Both ETBE and MTBE were also included in the blending matrix in order to reproduce realistic marketplace fuels.

The results are shown in Figure 2, where each point at a given ethanol content represents one of the 60 BOB samples specially blended for the study. The figure shows the delta.E70 of each ethanol/gasoline blend, which is the E70 of the ethanol blend minus the E70 of the gasoline BOB, plotted versus the ethanol content of the blend. Clearly, the impact of ethanol on the blend's distillation is substantial, as was shown for just one example in Figure 1. At 10% v/v ethanol, the increase in delta.E70 for the ethanol/gasoline blends ranges from 5 to 21% and the effect is even larger at higher ethanol contents.

In addition to the distillation behaviour of ethanol/gasoline blends, the study also evaluated changes in vapour pressure, the impact of small amounts of water on the blend's volatility and the molecular composition of the final blends. Predictive models for distillation properties were also developed based on regression techniques.

Because of the dramatic effects of ethanol on gasoline distillation, some refineries that typically manufacture BOBs having higher distillation properties can be expected to experience difficulties meeting the current volatility specification limits for 10% v/v ethanol/gasoline blends. For this reason, the responsible CEN Working Group is considering a CONCAWE proposal to relax the maximum volatility limits for 10% ethanol/gasoline blends. At the same time, two major vehicle test programmes, one by CONCAWE and one by the European auto industry, are in progress to investigate whether this relaxation will introduce any new emissions or driveability performance problems for current and future vehicles. Results from these studies are

Figure 2 Change in E70 distillation property with increasing ethanol content



The impact of ethanol on the blend's distillation is substantial; at 10% v/v ethanol, the increase in delta.E70 for the ethanol/gasoline blends ranges from 5% to 21% and is even greater at higher ethanol contents.

expected to be completed in time to inform CEN's technical discussions on E10 gasoline blends.

In addition to providing input to the current revision of the European gasoline specification, these vehicle studies will also set the stage for any future increases in ethanol content which may be needed in order to meet future aspirations of the RED and the NREAPs.

The European Commission's financial support of the BEP525 Study is greatly appreciated (TREN/D2/454-2008-SI.2.522.698). The study report, data and models are available for free download from the European Commission (http://ec.europa.eu/energy/renewables/studies/biofuels_en.htm) or CONCAWE (www.concawe.org) websites.