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UNIVERSITY OF WALES

Trinity Saint David

Update of European Summer Grade Gasoline Blending Models

DISSERTATION M6X00417

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1. Declaration of Authenticity

This dissertation is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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2. Executive summary

Pembroke refinery's gasoline blend focus team has requested an upgrade be carried out to the European blend stock for oxygenate blending summer grade gasoline EUROBOB_S. Due to the changing economics of the refinery and unit conditions, the original models built and tested in 2014 no longer adequately represent the component materials found in a grade of this type. Samples of summer grade gasoline have been retained during the summer of 2017, these samples will now be tested using the laboratory FTIR analyser. Once all the new spectra collected from the analyser are included in the model a topology review of the spectra will be carried out. A new model will be built and tested against neat samples which have previously been analysed and samples spiked with Platformate to mimic ethanol addition of 5 and 10 percent. All results will be appraised against data previously attained from the same samples. The model results will be presented to the blend focus team and then used by the online FTIR analysers to actively control and optimise EUROBOB_S gasoline blends. The expectation is these new models will drive down giveaway in EUROBOB_S blends which has increased over the years due to the recipe changes. At the conclusion of this project, the new models have been loaded into the online FTIR analysers and are functioning within specification, monitoring of each EUROBOB_S blend is being carried out by the CSE Specialist and the P&E Department to ensure the standard each blend is better than the previous models provided.

3. Acknowledgements

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Table of Contents

1.	Declaration of Authenticity	1
2.	Executive summary	2
3.	Acknowledgements	3
4.	List of Figures	6
5.	List of Tables	7
6.	Nomenclature	8
7.	Introduction	10
7.1	Overview of component products	12
7.1.1	Alkylate	12
7.1.2	Platformate	12
7.1.3	Isomate	13
7.1.4	Light and Heavy Cracked Naphtha	13
7.1.5	Ultra-Low Sulphur Gasoline	13
8.	Literature Review	14
8.1	Fourier Transform Spectroscopy	14
8.1.1	Beer Lambert Law	14
8.1.2	Infrared light Modulation	14
8.1.3	The Fourier Transform	14
8.1.4	Fourier Transform Spectroscopy	15
8.1.5	Michelson interferometer	16
8.1.6	Transept IV interferometer	17
8.2	Using Fourier Transform to obtain Spectrum from an Interferogram	18
8.3	Gasoline blending throughout history	19
8.3.1	Leaded gasoline	19
8.3.2	Methyl Tertiary Butyl Ether	19
8.3.3	Benzene, Toluene, Ethyl-Benzene and Xylene	19
8.3.4	Clean Octane Amendment	20
8.3.5	Ethanol	20
8.4	Cost of Quality	20
8.4.1	Prevention Appraisal Failure Model	22
9.	Gasoline Blending	24
9.1	Gasoline blending overview	24
9.2	Blending at Pembroke	25
9.3	The Blend Focus Team Requirements	26

9.4	Blend Optimisation	29
10.	Chemometric Modelling.....	32
10.1.1	Octane Number Laboratory Testing	33
10.1.2	Use of the Transept IV Interferometer.....	35
10.1.3	Laboratory Testing of BOB Specification Gasoline.....	35
10.1.4	Preparing Ethanol and gasoline Blendstock Hand Blends	36
10.1.5	Spectra capture via laboratory analyser	37
10.2	Experiment 1.....	43
10.2.1	Neat Sample #1.....	44
10.2.2	Neat Sample #2.....	45
10.2.3	Neat Sample #3.....	45
10.2.4	Neat Sample #4.....	46
10.3	Experiment 2.....	46
10.3.1	Spiked Sample #1	47
10.3.2	Spiked Sample #2	48
10.3.3	Spiked Sample #3	48
10.4	Management of Change.....	48
10.4.1	Human Factors within the management of change system.....	49
10.5	Upload of models to online FTIR analysers	51
11.	Timeframe	54
12.	Conclusion.....	55
13.	Recommendations	56
13.1	Short term: One month.....	56
13.2	Medium term: One – Six months	56
13.3	Long term: Six – Twelve months.....	56
13.4	Further work on this system.....	56
14.	Reference List.....	58
15.	Appendix.....	60
15.1	Preparing Ethanol and Gasoline Blend-stock Hand Blends	60
	Procedure LAB-WKI-030.....	60
15.2	Laboratory Testing of BOB Specification Gasoline.....	62
	Procedure LAB-PRO-003-A1	62
15.3	Manual Sample Collection System MSCS	63
15.4	Management of change Checklist Risk Assessment.....	70
15.5	FTIR Model Catalogue	74
15.6	2018 FTIR Models.....	76

4. List of Figures

Figure 1. Visual representation of the different blend modes.....	12
Figure 2. Simplest form of a Michelson Interferometer (Griffiths and De Haset, 2007)	17
Figure 3. Transept interferometer (Griffiths and De Haset, 2007).....	17
Figure 4. Fourier Transform from Interferogram to Spectrum (Zhao, J. 2014).....	18
Figure 5. RASCI chart for gasoline blending at Pembroke Site	26
Figure 6. Blend focus team organisation chart.....	27
Figure 7. Blend Optimiser Software Flow Diagram (Martin, A 2016).....	29
Figure 8. LIMS database with on specification EUROBOB_S, Octanes shown.	34
Figure 9. Site FTIR 'Transept IV' Interferometer (AIT, 2012).....	35
Figure 10. Laboratory automatic sampler and FTIR spectrometer in fume hood.	38
Figure 11. Sample spectrum for EUROBOB_S.....	39
Figure 12. Relevant regions of spectrum analysed	39
Figure 13. Spectrum modelling hotelling t^2 against Q residuals.	40
Figure 14. Spectrum modelling Leverage against Y Studentised residual.....	41
Figure 15. Spectrum modelling Y predicted against Y measured.	41
Figure 16. Final 2014 model of RON for EUROBOB_S.....	42
Figure 17. Proposed 2018 model of RON for EUROBOB_S	43
Figure 18. Valero Risk Matrix (Valero Energy Ltd, 2016)	49

5. List of Tables

Table 1 Recipe differences between 2014 and 2017	11
Table 2 Extract from Gasoline Blender Catalogue (Valero Energy Ltd, 2018)	25
Table 3 2017 example optimised blend	31
Table 4 Neat Gasoline Sample #1	44
Table 5 Neat Gasoline Sample #2	45
Table 6 Neat Gasoline Sample #3	45
Table 7 Neat Gasoline Sample #4	46
Table 8 Spiked Gasoline Sample #1	47
Table 9 Spiked Gasoline Sample #2	47
Table 10 Spiked Gasoline Sample #3	48
Table 11 Existing and new model names for EUROBOB_S grade gasoline	52
Table 12 Extract from April 2018 Blend Performance Review	52
Table 13 EUROBOB_S model upgrade timeframe	54

6. Nomenclature

ALARP	-	As Low As Reasonably Practical
API	-	American Petroleum Industry Gravity
ARA	-	Amsterdam Rotterdam Antwerp
BOB	-	Blend-stock for Oxygenate Blending
BTEX	-	Benzene, Toluene, Ethyl-Benzene and Xylene
CSE	-	Control Systems Engineering
CSR	-	Cold Storage Room
FCCU	-	Fluid Catalytic Cracking Unit
FTIR	-	Fourier Transform Infrared
HCN	-	Heavy Cat Naphtha
HF	-	Hydrofluoric Acid
iC8	-	Iso-Octane
ILB	-	In Line Blend
IR	-	Infrared
KPI	-	Key Performance Indicator
LCN	-	Light Cat Naphtha
LIMS	-	Laboratory Information Management System
MON	-	Motor Octane Number
MSCS	-	Manual Sample Collection System
MTBE	-	Methyl Tertiary Butyl Ether
nC7	-	Normal Heptane
NOX	-	Nitrous Oxide
ON	-	Octane Number
OPD	-	Optical Path Difference
PAF	-	Prevention Appraisal Failure

PPM	-	Parts Per Million
RASCI	-	Responsible, Accountable, Support, Consulted and Information
RFG	-	Reformulated Gasoline
R ²	-	Multiple Correlation Coefficient
RMSEC	-	Root Mean Squared Error of Calibration
RMSECV	-	Root Mean Squared Error of Cross Validation
RON	-	Research Octane Number
RDON	-	Road Octane Number
ROP	-	Refinery Operating Program
RVP	-	Reid Vapour Pressure
ULSG	-	Ultra-Low Sulphur Gasoline Unit
V/L	-	Vapour/Liquid ratio
VLI	-	Vapour Lock Index

7. Introduction

As a merchant refinery within a dominantly USA based company Pembroke Refinery is uniquely placed to be able to blend gasoline for any market in the world. Valero Energy Corporation is the world's largest independent petroleum refiner, a fortune 50 company based in San Antonio, Texas. With around 10,000 employees, Valero is an independent refiner and ethanol producer, with 14 refineries located in the United States, Canada and the United Kingdom and 11 Ethanol Production plants located in the Mid-continent region of the United States and approximately 7400 outlets carrying the Valero brand name. The company was created 1st January 1980, as a previously natural gas transportation business by the mid 1980's the company purchased a 50 percent interest in a Corpus Christi Refinery. In 1997 Valero started expanding by purchasing other refineries until 2011 when it purchased Pembroke from Chevron. With an overall refining capacity of 3.1 million barrels per day (Valero Energy Ltd, 2017).

The Pembroke refinery has had a gasoline blending unit since 1996 but at inception it was decided minimal optimisation would be required and for years only one property was manipulated, this property was Reid Vapour Pressure (RVP). In 2013 the company decided a project was required which would upgrade hardware in the field such as pumps, flow measurement devices (turbines) and control valves but also invest in new analyser hardware which would allow more properties to be used during the optimisation of a blend. One of the analysers which was added was a Fourier Transform Infrared (FTIR) analyser. This type of analyser shines a light through a sample of blended gasoline and depending on the spectrum gathered at the receiver it can indicate multiple properties such as;

Road octane number, Motor octane number, multiple evaporation temperatures and boiling points, and content of aromatics, olefins and benzene. All these properties have maximum and minimum limits within a specific recipe depending on where the gasoline will be used throughout the world. Models must be built for each property in a recipe so if the blend starts to deviate from the ideal recipe the optimiser can change the recipe to bring the blend back on specification. Throughout 2013 and 2014 every recipe blended at Pembroke was sampled and each sample was run through the laboratory FTIR analyser. From this information comprehensive models were built for each recipe to ensure the optimiser would function properly when required. A new project is now required because over the last 3 years the refinery and the gasoline blending within has changed. In 2014 a European summer grade gasoline (EUROBOB_S) could be best blended using the recipe shown on Table 1.

Table 1 Recipe differences between 2014 and 2017

	EUROBOB_S 2014	EUROBOB_S 2017
LCN LIGHT CAT NAPHTHA	35%	15%
HCN HEAVY CAT NAPHTHA	4%	4%
ALKYLATE	20%	12%
PLATFORMATE	22%	38%
ISOMERATE	15%	28%
BUTANE	4%	3%

Predominantly made up of LCN , Platformate, Alkylate, with minimal Isomerate, HCN and Butane included the 2014 recipe, this is significantly different to the 2017 recipe, due to the fact that each blend sample which was used to compile the EUROBOB_S grade models had only minimal Isomerate included and a large LCN content. As the recipes have changed this has had a major swing towards the same EUROBOB_S blend being predominantly Platformate and Isomerate heavy with only minimal LCN and Alkylate.

This has meant the refinery has started to see an increase in giveaway of some blends after completion and other blends being off specification completely. The objectives of this project will be to upgrade the current models used in the analyser house, used for analysing live gasoline as it is blended from its component parts, to eliminate off specification blends and minimize giveaway currently seen in some EUROBOB_S blends. Another aim of this project will be to provide these upgraded models using on site knowledge acquired by a Laboratory technician currently working in the engine laboratory at site and responsible for the laboratory analyser equipment, and the control systems engineering specialist responsible for overseeing the gasoline blending system from the advanced control standpoint.

Giveaway is caused when a property has a specification which is being minimised and the final samples result is high, for example if the Road Octane Number (RON) specified is 95.0 RON but the final tank sample is tested at 95.2 RON this means there is 0.2 octane numbers of giveaway in that tank and this could be a significant impact on the final value of the tank, it is then the refinery's decision to release the tank for export or re-blend and try and reclaim some of the giveaway.

Off specification blends are the opposite of giveaway this is when the final laboratory result does not meet the minimum requirement, for example 94.5 Road Octane Number. If the refinery has been contracted to supply 95.0 it cannot sell 94.5 and this tank must be re-blended before it can be exported, a visual representation is shown in figure 1.

During this project the refinery will be aiming to improve the quality and reliability of the gasoline blender by retaining EUROBOB_S samples taken from various blends and updating the existing EUROBOB_S models to include recipes with more versatility to how much of each component is included, to eliminate re-blends from the system and minimise the amount of giveaway seen in each EUROBOB_S blend.

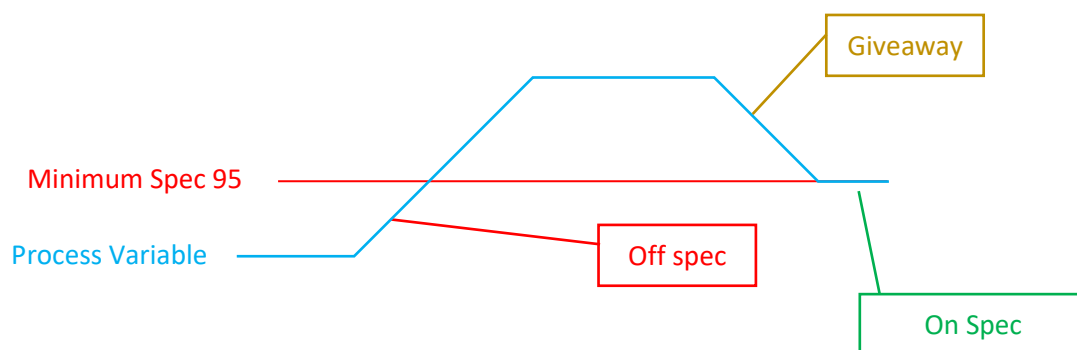


Figure 1. Visual representation of the different blend modes

7.1 Overview of component products

7.1.1 Alkylate

Valero Energy Ltd 2017 states - This product is produced in the Alkylation unit. The Alkylation unit is a catalytic process employing hydrofluoric acid (HF) as the catalyst. The process combines olefins with isobutene in the presence of HF acid to yield a product within the gasoline boiling range (Alkylate), this product consists of a mixture of hydrocarbons with high octane number RON=94.

7.1.2 Platformate

Valero Energy Ltd 2017 states - Heavy naphtha, consisting of paraffin's and cyclic naphthenes is fed from the Unifiner unit to the platformer unit. Platinum based catalysts are used as a bed and the hydrocarbon passed over the catalyst at high temperatures and in a hydrogen rich environment. Three catalyst reactors are arranged which enable them to convert the hydrocarbons to aromatics, increasing the octane. The unit has the capability to increase the octane number of the hydrocarbon from around 65 to between 98 and 102. The effluent from this also produces large volumes of hydrogen which can then be used in other refinery processes. The liquid product Platformate is stabilised in a debutaniser column to remove other impurities. Platformate can contain up to 10 percent benzene which must be removed to allow the Platformate to be used within the gasoline pool. The Platformate is distilled into light Platformate, benzene product and heavy Platformate in the benzene column.

7.1.3 Isomerase

Valero Energy Ltd 2017 states - The objective of the Isomerase unit is to take light naphtha feed from the Unifiner unit and Light Platformate from the platformer unit at around 70/30 ratio. The paraffins from the product are then converted to their respective Isomers. The unit then separates these Isomers into the Isomerase product. This can boost the octane number of the light naphtha from around 72 to 85.

7.1.4 Light and Heavy Cracked Naphtha

Valero Energy Ltd 2017 states – Light Cracked Naphtha (LCN) and Heavy Cracked Naphtha (HCN) Produced in the Fluid Catalytic Cracking Unit (FCCU) which takes feed from the vacuum distillation unit and crude distillation unit and using high temperatures the catalyst cracks the large hydrocarbons into lighter more valuable components, LCN and HCN. The reaction occurs when the catalyst is heated to 540°C and fluidised, during the hydrogen transfer reaction the olefin content is reduced, this helps the LCN and HCN to stabilise at this point the octane of the materials is also typically reduced. This reaction produces the high value LCN and HCN required for the gasoline pool.

7.1.5 Ultra-Low Sulphur Gasoline

Valero Energy Ltd 2017 states - The function of the ULSG unit is to reduce the sulphur content of the above naphtha streams to ensure the LCN and HCN used in the gasoline pool will conform to the current legislation's from around the world of how much sulphur content there can be in the final gasoline product. These values are currently 20PPM (Parts per Million) in Europe and 10PPM in the United States. The removal of the sulphur is carried out by combining hydrogen with the products and reacting them again through catalyst beds to produce products of less than 10PPM.

8. Literature Review

8.1 Fourier Transform Spectroscopy

8.1.1 Beer Lambert Law

'This law relates to the reduction in light intensity received at a detector after passing through a material be it gas, liquid or solid, due to absorbance.' (Daintith, 2008). Similarly 'the absorbance of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the absorption path length, l , and to the concentration, C , or — in the gas phase — to the pressure of the absorbing species'. (IUPAC, 2006).

It can be defined as:

$$A = \log_{10} \frac{I_0}{I} = \varepsilon c l$$

Where ε = Molar Absorption Coefficient

c = Concentration

l = Pathlength

I_0 = Incident light

I = Transmitted light

What this means is – a known light source passes a series of wavelengths of light through a sample cell housing and thus a solution. This Incident light is given the symbol I_0 . The detector receives the transmitted light after passing through the reference cell and this measurement is usually referred to as I (I for intensity). If I is less than I_0 it can clearly be seen the sample must have absorbed some of the light, this is given the symbol A .

8.1.2 Infrared light Modulation

'Broadband light contains many frequencies or wavelengths of light. Infrared (IR) systems separate broadband light into individual wavelengths (measured in cm^{-1})'. (AIT, 2012). Molecules absorb different wavelengths and by measuring this absorbance, the amount of those molecules or compounds present can be calculated and a model built.

8.1.3 The Fourier Transform

Named after the mathematician Jean Baptist Joseph Fourier, the Fourier transform is a method of transforming a function into another function. And can take the common form:

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$

With unitary normalised constants. In which t is time and i is the square root of -1.

'Lord Rayleigh discovered in 1892 that spectrum and its interferogram are related via a Fourier transform, and the first successful conversion of an interferogram to a spectrum was Fellgett who made the discovery over half a century later.' (Birkner, Wang, 2015).

8.1.4 Fourier Transform Spectroscopy

'The information that can be deduced from an infrared spectrum is complementary to that of other methods, and infrared spectroscopy provides valuable information that is unattainable by other methods. More important, however, a plethora of other applications became available with the advent in 1969 of the first commercial mid-infrared Fourier transform spectrometer with better than 2cm^{-1} resolution. These include quantitative analysis of complex mixtures'. (Griffiths and De Haseth, 2007). Infrared absorption spectroscopy is the method used to determine the structures of the molecules within a given sample. When a sample is exposed to infrared radiation the molecules of the sample selectively absorb radiation at specific wavelengths, which inherently changes the dipole moment of the sample molecules. While this is happening the vibrational energy levels of the molecules are transmitted from ground state to excited state. The frequency of this absorption peak is determined vibrational energy gap. By analysing the infrared spectrum information on the structure of the molecules can be obtained. What makes this type of analysis more useful is the capability of measuring gas, liquid and solid samples. Absorption radiation of most inorganic ions and organic compounds can be found within the region $4000\text{--}400\text{ cm}^{-1}$, thus this is the range of most FTIR analysers. (Birkner and Wang, 2018).

The three generations of IR Spectrometers;

1. The first generation IR spectrometer was invented in late 1950s. It utilizes prism optical splitting system. The prisms are made of Sodium Chloride. The requirement of the sample's water content and particle size is extremely strict. Furthermore, the scan range is narrow. Additionally, the repeatability is fairly poor. As a result, the first generation IR spectrometer is no longer in use.
2. The second generation IR spectrometer was introduced to the world in 1960s. It utilizes gratings as the monochromator. The performance of the second generation IR spectrometer is much better compared with IR spectrometers with prism monochromator, but there are still several prominent weaknesses such as low sensitivity, low scan speed and poor wavelength accuracy which rendered it out of date after the invention of the third generation IR spectrometer.
3. The invention of the third generation IR spectrometer, Fourier transform infrared spectrometer, marked the abdication of monochromator and the prosperity of

interferometer. With this replacement, IR spectrometers became exceptionally powerful. Consequently, various applications of IR spectrometer have been realized.

(Birkner and Wang, 2018).

8.1.5 Michelson interferometer

The general theory of interferometry can be understood best by first attaining an understanding of the way a Michelson interferometer operates to generate results from an infrared spectra.

The Michelson interferometer shown in figure 2, is a device that divides beams of radiation into two paths and then recombines them after a path difference has been introduced. Once this is done a condition is created where by the beams can have interference introduced to them, the variation of intensity received at the detector can be measured as a function of the path difference.

The simplest form of a Michelson interferometer consists of two perpendicular mirrors, one static and one able to move along an axis perpendicular to its plane. As well as these mirrors a beam splitter is also part of the system, this bisects the fixed mirror and the movable mirror allowing radiation from an external source to be partially reflected to the fixed source and partially transmitted to the movable source. Once the beams return to the beam splitter they interfere and are again partially reflected and partially transmitted. The intensity of the beams passing to the detector and returning to the source as a function of the path difference ultimately yields the spectral information in a Fourier transform spectrometer. Both beams, the one received at the detector and the one returned to the source hold equal information but in most cases only the information at the detector is of interest. There are choices as to how the movable mirror is adjusted, for a 'continuous scan interferometer' the mirror is moved at a constant speed, and for a 'step-scan interferometer' the mirror is held at equally spaced points for short periods and moved rapidly between these points. (Griffiths and De Haseth, 2007).

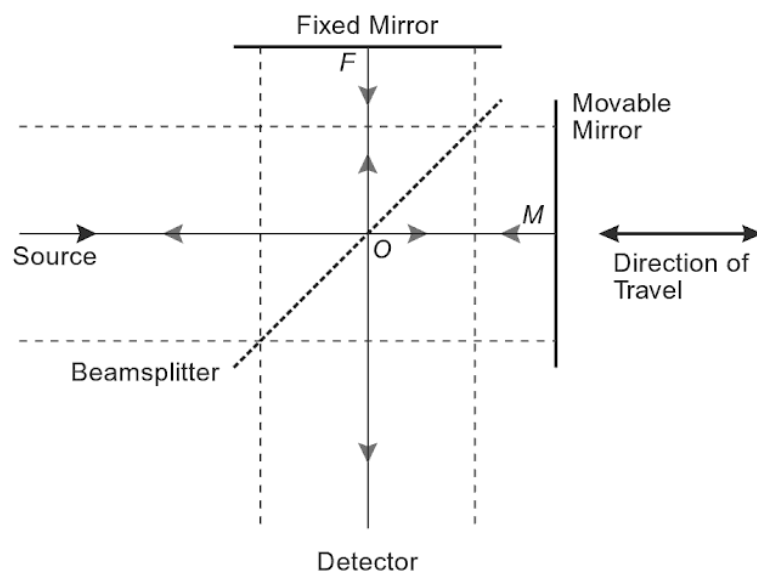


Figure 2. Simplest form of a Michelson Interferometer (Griffiths and De Haseth, 2007)

8.1.6 Transept IV interferometer

FTIR analyser's commonly use a Transept IV interferometer shown in figure 3, as opposed to the Michelson interferometer as described above. The difference between these two models of interferometer are primarily the transept model moves a refractive optical plate instead of a mirror. The beam splitter plates are wedge shaped, and the compensator plate of the beam splitter is scanned to increase the optical path of one arm of the interferometer.

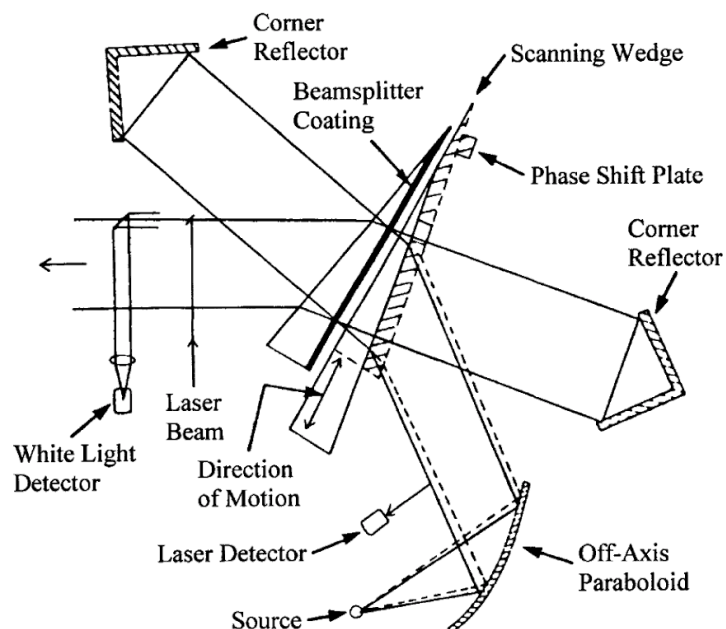


Figure 3. Transept interferometer (Griffiths and De Haseth, 2007)

A requirement for accurate motion control and measurement of the moving element can be reduced with the use of corner reflectors. With this design the interferometer achieves a modest amount of field widening and can show an improvement up to a factor of n^2 over the Michelson interferometer where n is the refractive index of the moving wedge. One drawback of a transept design over a Michelson design is the movement of the wedge, for a wedge angle of 10° the wedge must move around four times farther than the moving mirror of a Michelson design. (Griffiths and De Haseth, 2007).

8.2 Using Fourier Transform to obtain Spectrum from an Interferogram.

An interferogram is the resultant output once a sample has been analysed by the Interferometer, it is a function of time and the results make up the time domain. This time domain is then Fourier transformed to get the frequency domain, which can then be manipulated to provide a spectrum. Figure 4 shows an interferogram and its corresponding spectrum.

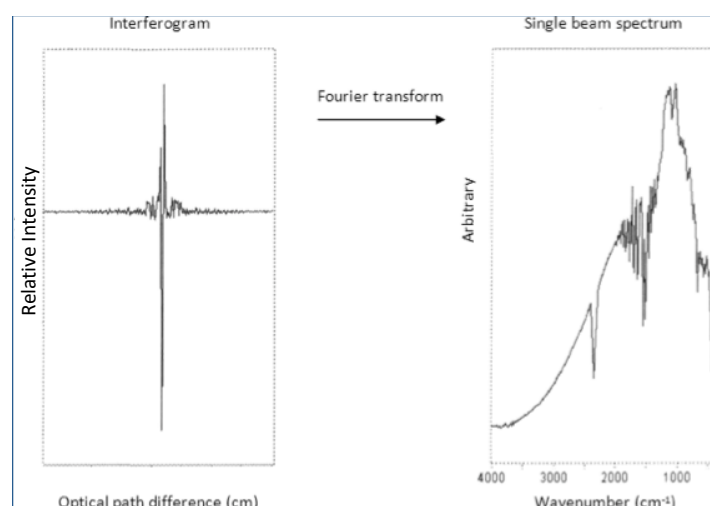


Figure 4. Fourier Transform from Interferogram to Spectrum (Zhao, J. 2014)

'The Interferogram obtained is a plot of the intensity of the signal versus the optical path difference (OPD) of the two signals. A Fourier transform of the interferogram can be viewed as the inversion of the independent variable of a function. Thus, Fourier transform of an interferogram can be viewed as the inversion of OPD. The unit of OPD is centimetre, so the invert of the OPD has the unit of inverse centimetre cm^{-1} . Inverse centimetres are also known as wave numbers. After the Fourier transform, a plot of intensity of signal versus wavenumber is produced. Such a plot is an IR spectrum. Although this explanation is easy to understand, it is not perfectly rigorous'. (Birkner, Wang, 2015).

8.3 Gasoline blending throughout history

8.3.1 Leaded gasoline

'During the early 20th century, automotive manufacturers were searching for a chemical component that had the capability to reduce engine knock. The discovery was made in 1921 by Thomas Midgley working for General Motors that – tetraethyl lead provided an octane boost to gasoline which in turn prevented engine knock' (Kitman, J. 2000). Stolark (2016) states, With lead's lower production costs than the other recently discovered octane enhancing components such as alcohols 'ethanol' and aromatic hydrocarbons 'benzene', this was the preferred method of controlling the engine knock observed during testing. Leaded gasoline became the predominant fuel type in Europe and the United States, until the Mid-1970s when the US and other governments began phasing out its use, because of proven serious health risks. Prior to this phase out the amount of lead used in gasoline was over 200,000 tons per year.

8.3.2 Methyl Tertiary Butyl Ether

Methyl Tertiary Butyl Ether (MTBE) – the use of reformulated gasoline (RFG), with the addition of MTBE to replace the octane boost seen while using lead, was mandated around 1990 in areas whose ground level ozone levels do not meet the set standard. According to Stolark (2016), RFG which has an increased oxygenate content to allow the fuel to burn more completely, was being used by the 1990s but questions arose with regard to MTBE's solubility in water after contamination of water courses in several States across the United States were attributed to MTBE. As of 2005 MTBE was being used in only small quantities for blending into gasoline and a vast reduction of reformulated gasoline being blended due to the increase in BOB being sort by the industry.

8.3.3 Benzene, Toluene, Ethyl-Benzene and Xylene

Benzene, Toluene, Ethyl-Benzene and Xylene (BTEX) – more commonly referred to as gasoline aromatics, are refined from low octane products into high octane components. According to Grey and Varcoe (2005), a small volume of these aromatics are inherent in the existing gasoline pool, they can be added as a boosting agent again to increase octane in the finished gasoline. At this point in the gasoline blending time line refiners had two alternatives an increase in refining capacity or the addition of ethanol to the gasoline. Refiners increased capacity to ensure BTEX components would be available. Once again BTEX came under warranted scrutiny when investigations found even very low exposure to the BTEX complex may contribute to – negative development, reproductive and immunological responses, as well as cardio-pulmonary effects. Small particles can be formed due to incomplete combustion of gasoline containing BTEX, these particles can be carcinogenic and mutagenic, and have

been linked to neurodegenerative disorders and cancers. Even with the removal of the benzene from the compounds may still have sufficient toxic levels.

8.3.4 Clean Octane Amendment

In 1990 in the US the Clean Air Act Amendments were passed, as part of these amendments S.1630 the Clean Octane amendment was enacted which gives the Environmental Protection Agency the authority to use “benign additives to replace the toxic aromatics that are now used to boost octane in gasoline”. (Stolark. 2016)

8.3.5 Ethanol

As stated above during the early years of the automotive trade manufacturers were interested in plant based alcohol fuels. Henry Ford designed the first model T to run on Ethanol. Gasoline at the time was a much cheaper fuel and control of this market was important, Standard Oil were quoted as saying ‘we are reluctant to encourage the manufacture and sale of a competitive fuel produced by an industry in no way related to petroleum’. (Grey and Varcoe, 2005). Today the majority of gasoline blended around the world has some Ethanol content denoted by the symbol E10 (for gasoline with 10 percent ethanol content) or E5 (5 percent ethanol content). A major advantage of using ethanol is its lower lifecycle greenhouse gas emissions as opposed to conventional gasoline. Again ethanol is an excellent octane boost provider. ‘Ethanol burns cleaner than petroleum based octane boosters. Studies have been carried out suggesting an increase from 10 to 15 percent ethanol in gasoline could result in a 6.6 percent reduction in cancer risk from tail pipe emissions’. (Unnasch and Henderson, 2014) Contradictory to this there is evidence that ‘increasing ethanol in gasoline increases Nitrous Oxide (NOX) emissions, which is an ozone precursor. Other studies find either no relationship between ethanol addition and NOX emissions, or a decrease in NOX emissions with the addition of ethanol’. (Maricq et al, 2012).

8.4 Cost of Quality

‘The cost of quality was found to account for between 5 and 25 percent of sales revenue’ (Williams, et al. 1999). Quality can be defined best using the three common definitions asserted by Thorn (2016).

Conformance to specification – a buyer takes the view that the product or service being purchased will conform to some specifications.

Fitness for purpose – focusses on the performance of the product or service being purchased during its primary function.

Conformance to requirements – the products or services being purchased should satisfy the expectations of the customer, this definition places the greatest emphasis on the customer.

Equating the above definitions to a gasoline blending system it can be found there are many customers during the cycle to deliver gasoline.

Conformance to specification, the oil trader will sell a cargo of gasoline for delivery on a certain date. There are now two customers from the view point of the Purchasing and Economics (P&E) department, the trader has sold a cargo of a specific gasoline for delivery on a certain date, the trader is expecting this gasoline to be blended and on specification ready for the ship when it docks to avoid Demurrage and late delivery charges. The final product customer is also expecting the grade of gasoline specified in the sale so the conformance to specification must be correct else the customer might be lost to a competitor who can deliver the correct grade of gasoline on the correct date. If customers are lost through non-conformance to specification this could lose the company millions of dollars of future revenue.

Fitness for purpose, the grade specified at the start of the blend should be checked by the panel operator before the blend is started and verified with the P&E department to ensure no mistakes have occurred, grade names can be similar, EUROBOB_S and EUROBOB_W could be mixed up and a winter grade gasoline blended which would fail some vital tests during laboratory testing and may mean a whole tank of gasoline needs to be slopped back to the crude unit feed or the tank certified off specification and the contents only used during other blends but at very low volumes, normally between 5 and 10 percent per blend. With a full tank of gasoline equating to 20,000m³ this could mean the tank being off specification for an extended length of time, again a large expense to the company for not delivering a quality product.

Conformance to requirements, as most of the gasoline from Pembroke site is exported to the United States (around 60 percent) great care must be taken when analysing the laboratory samples as a failure of the product when it is analysed after travelling across the Atlantic ocean would require either a downgrade of the gasoline sold which would still mean a sale but for a lesser gasoline price or a shipment being returned to site and pumped back into shore tanks, the majority of gasoline ship batches require three on specification tanks to fill the ship. Taking delivery of an off specification ship could mean taking three gasoline shore tanks out of service and with only seven gasoline tank available this would mean at least a slowdown in production for the rest of the site due to the fact that ullage of gasoline tanks was full and with nowhere to blend the component tanks to.

8.4.1 Prevention Appraisal Failure Model

'Prevention-Appraisal-Failure (PAF) model is the most closely studied by researchers and the most commonly used in practice'. (Plewa, Kaiser and Hartmann, 2016)

Quality costs can be divided into four areas:

'Prevention costs – costs associated with planning and operation of a quality management system to reduce the failure and appraisal costs'. (Thorn, 2016). In a gasoline blending system, these costs can be mainly associated with the P&E department ensuring when they receive a blend from the trading department they will have enough components which will be required for this blend. Training of operations personnel on the different systems within the gasoline blending environment, Manual Sample Collection System (MSCS), the blend optimiser etc. At this stage there should also be some consideration of the cost of the operators required to start and run the blend correctly, time requirements for the blend and ship loading to avoid demurrage.

'Appraisal Costs – costs associated with the verification activities to ensure conformance requirements'. (Thorn, 2016). The laboratory technician's time to carry out testing of ILB samples of online gasoline blends, and final tank samples once a blend is completed. Cost of the preventative maintenance of the online analysers to ensure maximum uptime carried out by the analyser department.

'Internal Failure Costs – costs associated with non-conformance of the product or service prior to the customer receiving them'. (Thorn, 2016). Off specification gasoline once the blend has finished and the samples tested in the laboratory. This would lead to, at worst, sending the whole tank to slop. A more realistic outcome would be a downgrade in gasoline grade sold or a re-blend of the tank to attempt to get the product on specification, this can only be carried out if a sufficient ullage is available in the tank, ullage is the amount of space left between the product in a tank and the maximum safe working height of said tank. During an issue like this a loss of capacity as stated above will be felt. At this point the cost of retesting in the laboratory will also need to be accounted for.

'External Failure Costs – costs associated with the non-conformance of the product that are detected by the customer'. (Thorn, 2016). All products are released for shipping by the onsite laboratory at Pembroke, but for blends travelling to the United States the final testing is carried out at 'Disport' (after shipping and unloading to shore tanks), so retained samples are stored to ensure further testing can be carried out if required. If samples are certified off specification at disport this would be an external failure, the company could have a loss of market share. There may even be a return of goods.

There are also five stages to the PAF model. Taking the upgrade of the EUROBOB_S model in isolation and explaining the five stages it is seen that;

Sell – over the past 4 years the blend focus team has done a good job of selling the importance of minimising giveaway and eliminating off specification blends or actively driving down the cost of quality via the use of the models within the analysers and thus the optimiser.

Information – the blend focus team have been able to locate problems with the system quickly and work to eliminate them quickly. More on this team in chapter 9.2.

Measurement – the P&E department have been able to identify which grades of gasoline have seen the largest changes from the 2014 models and asked the team to focus on these grades as a priority.

Analysis – new grades of EUROBOB_S have been retained to ensure they can be added to the existing pool of data and used to enhance the existing model.

Action – the company have actively supported the update of these gasoline models to ensure the cost of quality will not suffer due to neglect of the models, for the first time this year the company have also provided funding for this project.

Although the PAF model states there is a limit to quality improvement with relation to cost small projects like this ensure the gasoline blender will keep optimising the product being sold.

9. Gasoline Blending

9.1 Gasoline blending overview

For many years gasoline has been blended 'neat' this means the final product delivered from site is an oxygenate-free product. Blending neat gasoline for any market was a difficult and well-regulated task, but the predicted property outcomes could be calculated to acceptable tolerances in a simple spreadsheet.

With the inclusion of an oxygenate (ethanol), 'Oxygenates which have received substantial attention as gasoline blending agents include, but are not limited to, methanol, ethanol, tertiary-butyl alcohol, methyl tertiary-butyl ether, ethyl tertiary-butyl ether and methyl tertiary-amyl ether. However, ethanol has become one of the most widely used oxygenates'. (Carpenter et al., 2010). The gasoline will acquire an octane boost, and is a more economical source of this boost than a standard hydrocarbon like Alkylate or Reformate, the boost now needs to be predicted during blending as inclusion of the ethanol cannot be done during the blending task. The reason for this is, ethanol is water soluble and as a consequence of this water solubility an ethanol blended gasoline could undergo unwelcome changes such as absorption of water which will then be present in the gasoline at the distribution point. Due to this problem ethanol is usually added to the blend stock at a point as near to the end of the distribution system as possible. Gasoline which is blended to include ethanol is commonly referred to as Blend-stock for Oxygenate Blending (BOB). Common blend-stocks made include RBOB (reformulated BOB), CBOB (conventional BOB), CARBOB (Californian reformulated BOB), CAN_CBOB (Canadian Conventional BOB) and EUROBOB (European BOB). The ethanol content of the previous BOB's differs from 4.8 percent to 10 percent and in the future there will be a drive towards 20 percent throughout the world, this means these blends will need reviewing periodically or when a significant change in the recipe composition has taken place.

'The modification involves the use of chemometric models that predict the oxygenate containing finished gasoline properties from spectroscopic data for the xBOB' (Carpenter et al. 2010). These models are used by a variety of analysis instrumentation along with a large closed loop control system which makes adjustments as required to the ratio of each component being used by the control system to blend the BOB gasoline. Once a blend is completed samples are taken from the blended tank to the laboratory and tested against the specifications for the finished gasoline, this means the required quality and quantity of ethanol is hand blended into the BOB, the procedure for this can be seen later in part and completely in Appendix 15.2. If the sample is on specification, a certificate of quality is issued and the

tank is released for export to whichever distribution system is required be it ship, pipeline or road tanker.

9.2 Blending at Pembroke

‘A small reduction in giveaway yields impressive results; for a typical refinery, blend optimisation could deliver millions of dollars per year in bottom line savings. It is estimated that the industry-wide total costs of RVP and octane giveaway exceed 2 Billion dollars a year in the US and several times that total worldwide. Capturing even a fraction of that opportunity can offer a strategic refining advantage.’ (Scriven, Seiver and Martin, 2016)

Within Pembroke Refinery the BOB gasoline is blended in line with the method shown above. The refinery currently has the capability to blend neat finished gasoline, and anything between 4.8 percent and 10 percent Ethanol content BOB’s including all listed above. Ethanol has also become the standard oxygenate used for BOB’s made at Pembroke for the European market and the export grades to the United States of America. A commonly blended BOB at Pembroke is EUROBOB_S blend-stock which has been blended at the site regularly since 2013, the suffix S stands for summer, there are 3 standard EUROBOB blends made at the site summer (S), inter (I), and winter (W) a reduced version of the product catalogue is shown in Table 2 (Full Catalogue in Appendix 15.5). Chemometric models were built for each property measured, within each recipe during start-up of the upgraded gasoline blender in 2013/14. The models have been reliable at returning on specification gasoline with minimal giveaway during this time. In late 2014 the Alkylation unit deflourination upgrades came online which yielded consistent low RVP alkylate, this in turn helped in creating a new recipe construct for EUROBOB_S. With the reduction of LCN and Alkylate in favour of an increase in Platformate and Isomerase. These changes while still blending together to give an on specification EUROBOB_S mean the chemometric models currently being used to optimise the blend are not ideal as they do not contain the same ratios of components as what the blending system is trying to use.

Table 2 Extract from Gasoline Blender Catalogue (Valero Energy Ltd, 2018)

FTIR CODE	GASOLINE PRODUCT ID (Gasoline Grade)	SEASON	FUEL TYPE	% ETOH	Research Octane #	Motor Octane #
5	EUROBOB-S Sub-Octane Premium Gasoline	SUM	Euro BOB	4.8	BLENDED EB_Sum_ROM S: 95.0 MIN	BLENDED EB_Sum_MON S: 85.0 MIN
6	EUROBOB-60 60-KPA Sub-Octane Premium Gasoline	SUM	Euro BOB	5.0	BLENDED EB_Sum_ROM S: 95.0 MIN	BLENDED EB_Sum_MON S: 85.0 MIN
7	EUROBOB-I Sub-Octane Premium Gasoline	INT	Euro BOB	4.8	BLENDED EB_Win_ROM S: 95.0 MIN	BLENDED EB_Win_MON S: 85.0 MIN
8	EUROBOB-90 90-KPA Sub-Octane Premium Gasoline	WIN	Euro BOB	5.0	BLENDED EB_Win_ROM S: 95.0 MIN	BLENDED EB_Win_MON S: 85.0 MIN
9	EUROBOB-W Sub-Octane Premium Gasoline	WIN	Euro BOB	4.8	BLENDED EB_Win_ROM S: 95.0 MIN	BLENDED EB_Win_MON S: 85.0 MIN

The blending system relies on a range of analysis instrumentation to give online feedback of the gasoline currently running through the header, the analysers include: - 2 off Grabner analysers which measure Reid Vapour Pressure (RVP) and Total Vapour Lock (TVL) a Density analyser, and 2 off Fourier Transform Infrared (FTIR) Analysers measuring a range of properties including Research Octane Number (RON), Motor Octane Number (MON), temperature limits, evaporation limits and percentage Olefins, Aromatics and Benzene. It is the FTIR analyser models which will be upgraded during this project.

9.3 The Blend Focus Team Requirements

The blend focus team was setup at the end of the commissioning phase of the new gasoline glender at Pembroke, to meet once a week and discuss the current week's blends and how well they performed and review any issues with the system and set actions on the correct department to get these issues resolved in a timely manner. The team consists of a Control System Engineering (CSE) Specialist, dealing with the control systems running the blending optimiser, P&E Department, the person who prepares each recipe of gasoline to be blended, laboratory personnel, responsible for laboratory testing, analyser department, responsible for the maintenance of the analysers used to run the blender and an operations advisor, who liaises between the focus team and the operations personnel running the blender. The P&E department have seen a reduction in the reliability of the EUROBOB_S blends over time, meaning more product is being sold with giveaway. The average octane giveaway on gasoline blends in 2017 at Pembroke site was \$801,000. (Seiver, 2017)

Task	CSE Engineer	P&E Scheduler	P&E Manager	CSE Manager	Operations Advisor	Panel Control Operator	B&S STL	Operations Business Manager	Blender SME	Analysar Technician	Lab Technician	Instruments	IS Applic
Prepare blend recipe	C	R	A										
Download blend recipe	C	R	A										
Check recipe and adapt in BOSS (if required)	C	R	A										
Inform operations and provide additional blend information		R	A										
Start blend						R	A						
Troubleshoot analyser issues online	I	I							R				
Test ILB samples during blend and upload results to LIMS					C					R			
Accept LIMS results imported into BOSS application					R	A							
Make adaptations to the blend online in order to keep BOSS in a feasible state	C	S			I	R	A						
Stop blender and release blend when complete					R	A							
Document any issues that arise during the blend	I	I			I	R	A			I	I		
Test final blended tank and upload results to LIMS										R			
Review finished blend quality	I	R	A										
Order and prepare reblend (if required)		R	A										
Assign actions to resolve any issues that affected blend	S	R	A	I	I			I	I	I	I		
Weekly blender meeting	S	R	A	I	S		C	I	I	I	S	S	
Assign long term actions to improve blender performance	S	R	A	I	S			I	I	I	S	S	
Gather historic blend performance data	R	S		A									
Prepare monthly blend report	R	S	I	A	I			I	I	I	I		
Weekly blend issues log	S	R	A	I	S			I	I	I	S	S	
FTIR modelling	R	I		I				C	C	C	R		
Analysar performance and biasing	S	I			I			C	R	S			
BOSS application	R	I		A	I	I		I					R
Bixby application	C	I											
DeltaV digital blender	R	I		A	I	I	I	I					
MBO	R		A										
Analysers	S	I			I	I	I			R	S		
LIMS	C	C									R		S
Ops training	C	I			R		S	A					
Metering	S	I			I							R	

Figure 5. RASCI chart for gasoline blending at Pembroke Site

Once the original project was completed a Responsibility matrix, Responsible, Accountable, Support, Consulted and Information (RASCI) was configured to ensure each person within the focus team knew their roles, shown in Figure 5 with the Control Systems role highlighted.

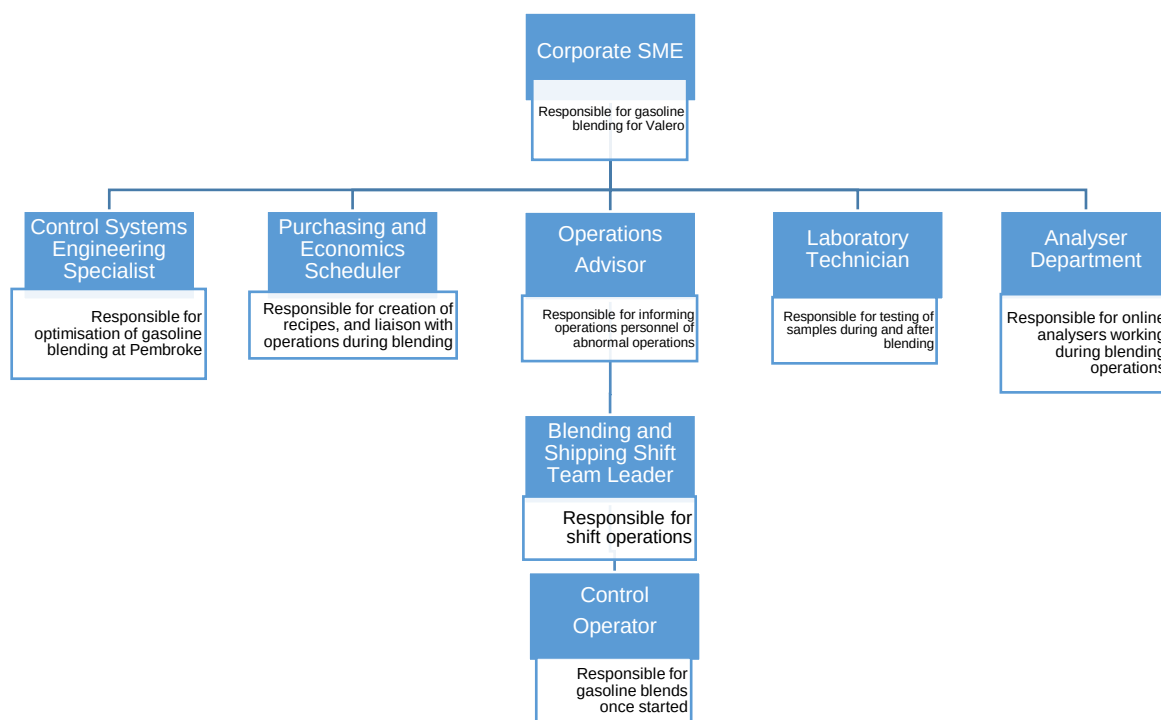


Figure 6. Blend focus team organisation chart

The role of CSE specialist within this team has changed since 2014, during the initial installation of this system the CSE specialist was the first point of contact for problems seen by the control operators due to the newness of the system and the broad knowledge which the CSE specialist possessed. Once the system was running smoothly direct responsibility for chairing the meetings and overseeing the blender was moved to the P&E department to align with the corporate model.

One Key Performance Indicator (KPI) used at site and reported corporately is, based on the functionality the site currently has, this 'Site Capability' at Pembroke is 0.29 Octane Numbers with a 2017 average of 0.32ON.

This figure is obtained by starting with the historic average across the company of 0.35ON coupling with this variability of an optimiser of around 0.05ON and on-line certification with an acceptable target of 0.05ON this means the lowest reasonable target is 0.1ON above the specification.

Utilising an advanced process control (APC) optimiser, such as the one at Pembroke, an improvement of -0.10ON can hope to be seen.

There is another bonus added for Pembroke as around 30 percent of blends were historically re-blended to meet specification requirements this bonus is shown below.

Bonus = Base – (%re-blends*0.15 + (1-%re-blends)*Base Giveaway (0.35 or 0.25 with APC)

Bonus = 0.25 – (30% * 0.15 + (1-30%) * 0.25)

Bonus for Pembroke = -0.03

There is a penalty used for sites which commonly make small or multi blends, this also applies to Pembroke because at times to overcome ullage issues, where the component tankage is very full and limited storage and the process units are still online, gasoline is blended without knowing what the final grade will be, these blends are commonly called inter blends. When the P&E department at Pembroke was asked they worked out anything up to 50 percent of blends could change octane grade and thus octane specification during a blend. For this a penalty of 0.05ON is used

The final penalty awarded to Pembroke is due to the fact the site is able to blend gasoline direct to ships saving time and shore tank usage, but ultimately buffering the octane value of these cargos because once on the ship it is much harder to correct, a penalty of 0.02 is placed on the total.

When totalled together the site capability is:

Base	+ (-APC)	+ (-trim control)	+small blend penalty	+ direct to ship penalty
0.35	– 0.10	– 0.03	+ 0.05	+ 0.02 = 0.29ON KPI

(Seiver, D. 2017).

The average site capability for 2016 and 2017 has been 0.32 which equated to around \$504,000. The Blending focus team at Pembroke have decided EUROBOB_S models should be the first set of models addressed by inspecting the current models within the system and also retaining samples of current EUROBOB_S blend-stock at the onsite laboratory. These samples can then either be added to the existing EUROBOB_S models to make a more robust model which include different styles of recipe or used to make a new model for EUROBOB_S which eliminates the old models from the system. Once enough samples have been entered into the software and a comparison can be made the results can be shown to the blend focus team and a decision made as to a clear path forward.

9.4 Blend Optimisation

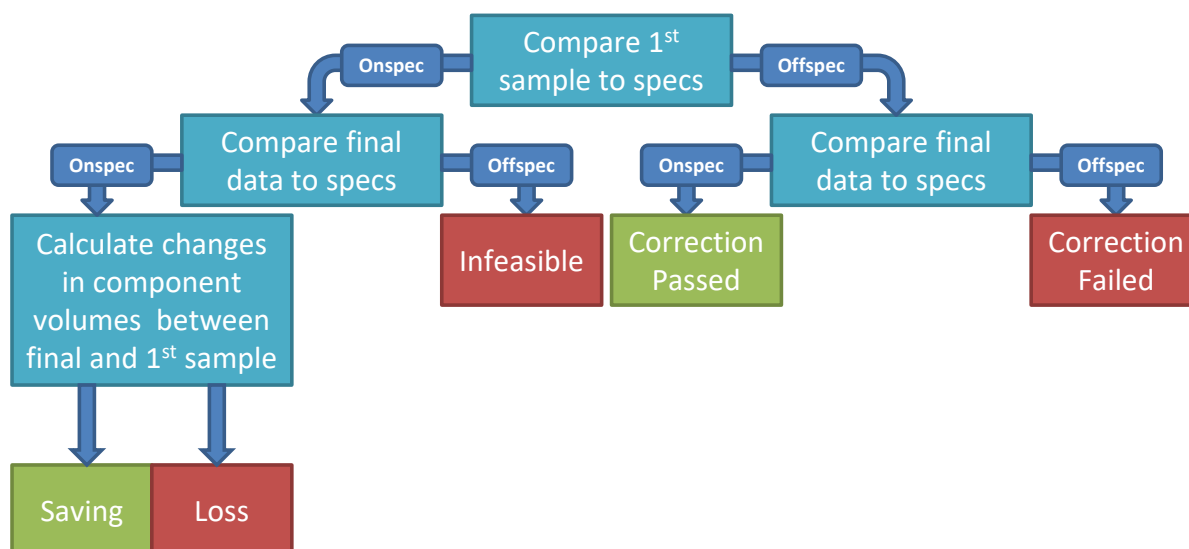


Figure 7. Blend Optimiser Software Flow Diagram (Martin, A 2016)

Figure 7 is the control flow chart for the gasoline blending optimiser. These are the steps the optimiser goes through each time a blend is performed. Starting from the top after one hour of blending without the optimiser moving the initial blend ratios the field operator will take three in line blend (ILB) samples from the MSCS in the analyser house, these samples are taken in brown one litre laboratory sample bottles.

Once this sample has been drawn the optimiser will use the online analyser data to determine if the first sample is on or off specification. If the first sample is off specification the optimiser's only job for the remainder of the blend is to adjust the components to ensure the blend finishes on specification. If at the end of the blend the final sample is on specification this is classed as a correction passed – a positive solution as the optimiser prevented the tank needing a re-blend. If at the end of the blend the final sample is off specification this is classed as correction failed – a negative solution as the optimiser was unable to prevent the tank from requiring a re-blend.

Optimiser objectives – the optimiser can manipulate the components volumes and ratios being input to the blend on feedback from the FTIR and RVP analysers, but it must have constraints to work within. There are three optimisation objectives which can be set for each blend.

Minimise component cost (C/c) – if this is set, denoted by a capital C, the optimiser will use the cost of each component and remove high value components in favour of lower cost components that can provide the same properties required for that blend.

Minimise deviation from target ratio (R/r) – if this is set the optimiser will constrain each component ratio and only move the target ratios a small amount from each initial ratio.

Minimise Quality giveaway (Q/q) – if this is set the optimiser will manipulate the component ratios to minimise the deviation of the maximum or minimum settings for each property being analysed within the current blend.

These objectives are commonly left set as 'CrQ' denoting the requirement for the optimiser to minimise the component cost, ignore the deviation from the target ratio and minimise the quality giveaway.

If the first sample is on specification the optimiser is now free to manipulate the blend to ensure the tank stays on specification but also minimises cost and giveaway. If at the end of the blend the final sample is off specification this is classed as an infeasible blend – a negative solution as the optimiser actively moved the blend to an off specification position during the blend.

If at the end of the blend the final sample is on specification another calculation is carried out and each manipulated component volume or ratio is checked against the initial recipe and the final recipe. From this a saving due to the optimiser can be found – a positive solution for the blender, but after the calculation it may also be seen that due to using more of a high value product to minimise quality giveaway the blend could also make a loss – a negative solution for the optimiser.

As well as the optimiser carrying out this for each blend the P&E department are also carrying out multi blend optimisation forecasting at between 10-14 days ahead, so constraints are also placed on each blend to ensure the optimiser does not use all of one component in a blend which will be needed for the proceeding two to three blends.

With the current market price for export gasoline on the gulf coast of the United States at around \$1.76 per gallon, 42 fluid gallons in a barrel the market is around \$73.92 per barrel, with high value components within the blend stock with prices around \$71 per barrel for Alkylate and \$75 per barrel for Platformate, minimising the use of these components and replacing them with low value products such as butane with a cost of \$25 per barrel, means each blend can make a substantial saving if the replaced components still yield an on specification final gasoline product. Although around 60 percent of gasoline blended at Pembroke is exported to the United States there is still a significant percentage sold to Europe. The EUROBOB_S market price for north west Europe, calculated on the Amsterdam-Rotterdam-Antwerp (ARA) bunkering figures, these figures account for more than 25 percent of Europe's total oil product imports so is used as a benchmark for European product pricing, as stated by Snyder and Halling, the current price of EUROBOB_S gasoline according to the ARA is \$82 per barrel, so could be seen as a more favourable region to export gasoline too but the much bigger shipping tankers that can cross the Atlantic ocean mean more high value product is currently exported to the United States but from a batch by batch blending

standpoint there is more to be gained by optimising blends being sent to Europe as the margins will be higher. Savings of over \$120,000 per blend have been seen during the summer of 2017 on multiple EUROBOB_S blends with as little as 2 percent overall change to the recipe sent down by the P&E department. An overview of the changes made by the optimiser can be seen in Table 3.

Table 3 2017 example optimised blend

Product	Initial ratio %	Final ratio %	Difference %	Product cost \$/bbl	Volume bbl (increase)
Alkylate	13.5	13.1	0.4 ↓	75	3446
Butane	2.2	2.1	0.1 ↓	25	402
Isomerate	14.8	16.8	2.0 ↑	51	(19448)
LCN	32.2	34.8	2.6 ↑	52	(24513)
Platformate	37.4	33.2	4.2 ↑	75	40120

Replacing Alkylate and Platformate at \$75/bbl during this time with Isomerate and LCN at \$51 and \$52 respectively yielded a saving on an 113,000 barrel blend of just over \$120,000.

Another factor which must be considered when optimising gasoline blends for shipping tanker export is demurrage. Demurrage is the charge payable to the owner of a chartered ship after failure to load or discharge the ship within the time agreed. Each ship which is berthed at Pembroke and is loaded with gasoline has been scheduled for; arrival, loading – normally standard 36 hours for shore tanks to ship - and departure. If the ship arrives on time and is berthed the loading timer is started, for ships that arrive late the demurrage charge is normally waved but if berthed on time and the loading is not as quick as planned a demurrage charge is made by the ship's owner to the refinery from the first hour after the timer expires, as the ship is only making money for the owner when it is at sea. This demurrage charge can vary depending on the owner but is normally in the range of \$18,000 per day so around \$750 per hour, ideally having two shore tanks finished and on specification before the ship is berthed means while these two tanks are discharging to the ship the third tank can be blended and sampled before it is required. The optimisation of a shore tank can be the difference between the ship loading on time or not.

Other factors used for deciding if a blend should be optimised or not is the size of the batch being blended. As an ILB run through the laboratory engines can take up to an hour for the results to be produced and sent back to the optimiser, sometimes smaller blends are not

optimised. A batch of 10,000 m³ blended at a rate of 1500m³/hr will have its first sample taken one hour into the blend, results will not be produced for another hour. The optimiser will then use these results to verify the online analysers and make adjustments if necessary and back casting errors for the total time blended. The next sample would be due for drawing at hour five and results would come at hour six but at this time there would only be one hour left on the blend which would not be enough for the optimiser to correct a problem, so the site standard is to not optimise any batches less than 10,000m³.

Pembroke also have the capability to blend gasoline direct to the ship. On average around three direct to ship blends are carried out at the site each month, this allows the P&E department more flexibility with the shore tanks, having the capability to blend a high octane gasoline direct to the ship means the shore tanks do not have to receive high octane product in them and then 'turn the heel' of the tank back to low octane which historically can take several blends to rectify each having unavoidable giveaway. One drawback to direct to ship blending is the lowered flowrate achievable via this method. For tax purposes each batch leaving the refinery needs to be metered through highly accurate and proven flowmeters, and loading arms which also have maximum flowrates which cannot be exceeded. For the berths at Pembroke this maximum is between 900-1000m³. So this must be taken into account when planning large direct to ship blends as there is a real chance at such low flowrates that component tankage ullage will be decreasing while the blend is running and with the gasoline blender being used direct to the ship, there is no way to move component product to finished gasoline tanks. The largest cargo blended direct to ship to date from Pembroke is 320,000 barrels (~51000m³) a blend which took over 50 hours to complete and saw a saving for the refinery of around \$145,000.

All of the above must be considered when deciding to optimise each gasoline blend at site, and only through the experience of multiple people within the blend focus team can the optimiser mean of 85 percent of all blends at site be maintained.

10. Chemometric Modelling

The Pembroke Laboratory Information Management System LIMS is used by all laboratory technicians to enter results of tests performed on specific samples of product. With the vast array of samples delivered to the laboratory throughout a 24 hour period a robust sample numbering system is required. Operators print sample labels before drawing a sample from the MSCS within the analyser house, they collect three off brown, one litre bottles of blended gasoline attach the labels to the bottles and deliver the samples to the laboratory as quickly as possible. When printing the label the LIMS application will assign the sample a unique sample number this number will be tied to the sample forever and makes it possible to retain

samples for a considerable lengths of time to ensure repeat tests can be performed if there is a query on the quality of the gasoline delivered to the customer. The results for these samples are also retained in LIMS and it is these results and the retained samples which can be used to test the existing models for the FTIR and the proposed new models built during this project.

A visual representation of the MSCS can be seen in the appendix 15.3 of this document. But the general procedure operations follow during an ILB sample draw is as follows.

1. Ensure the sample bottles being used are clean and dry. Place the first bottle firmly into the sample chamber.
2. Product is circulated through the system to ensure a representative sample of the gasoline going through the blender at the time of sample is correct. Ensure flow meter and pressure gauge values are within acceptable limits.
3. The product is cooled through a shell/tube chiller. A positive flow should be observed via a rotating vane within a sight glass.
4. The piston within the volume chamber is forced upward drawing product into the volume chamber. Once full and sufficiently chilled automatic valves will actuate and allow the sample to flow to the sample container (brown bottle).
5. Once full the sample bottle can be removed from the sample chamber and the procedure repeated two more times.
6. Once complete sample bottles should be stored correctly and moved to the laboratory as quickly as possible for testing.

10.1.1 Octane Number Laboratory Testing

Within the site laboratory a large section of the building is given up to the engine lab. Contained in this laboratory are three single cylinder engines used primarily for measuring the RON and MON of finished gasoline samples and a host of other component products as required, having three ensures redundancy in test equipment as one is always testing RON, one is always testing MON and one is kept in a state where it can easily be converted to measure either required test. The Octane Number (ON) of a fuel is measured in these test engines, and is defined by comparison with a mixture of iso-octane (iC8) and normal heptane (nC7) which would have the same anti-knocking capacity as the fuel being tested. The ON is derived from the percentage, by volume, of iso-octane in the mixture. For example, a gasoline with a knocking characteristic the same as a mixture of 90 percent iso-octane and 10 percent normal heptane would carry an octane rating of 90RON. The test is run on a single cylinder, variable compression ratio engine (4:1 to 18:1 range). The test fuel is run in the engine starting as low compression ratio and gradually increasing it. At the point where knocking starts the

compression ratio is compared to the standard fuel (iC8/nC7 mixture) that starts knocking at that ratio and then the Percentage of iC8 in that standard fuel determines the ON of the fuel.’ (Chevron Energy, 2009). ‘Three types of octane numbers are commonly referred to Research, Motor and Road. Research represents low speed engine operation (600 RPM on test engine), Motor represents high speed / heavy load engine operation (900 RPM on test engine) and Road represents the average of the two’. (Chevron Energy, 2009).

Samples									
Sample #	Draw Date	Draw Time	Sample Status	Approval status	Plant Code	Material Code	Sample Point	Sample Type	Batch
595675	11/05/2017	15:15:00	Tested-OK	Verified-OK	B&S	EUROBOB-S	N/A	FINAL	GASO

Draws			
Tag No	Draw Type	Container	Status
1	COMPOSITE	1L BROWN BOT	Tested-OK
2	COMPOSITE	1L BROWN BOT	Tested-OK
3	COMPOSITE	1L BROWN BOT	Tested-OK
10	ETHANOL-B	1L BROWN BOT	Tested-OK
20	UPPER	1L BROWN BOT	Tested-OK
21	MIDDLE	1L BROWN BOT	Tested-OK
22	LOWER	1L BROWN BOT	Tested-OK
23	SUCTION-LE	1L BROWN BOT	Tested-OK
30	UPPER	1L BROWN BOT	Tested-OK
31	MIDDLE	1L BROWN BOT	Tested-OK
32	LOWER	1L BROWN BOT	Tested-OK
50	UPPER	1L BROWN BOT	Tested-OK

Test Results					
Test	Analyte	Entered Value	Display Val	Status	Average
D2700-MON	MON	84.5	84.5	Done	
D2700-MON	MONc	84.3000	84.3	Done	
D2699-RON	RON	94.0	94.0	Done	
D2699-RON	RONc	93.8000	93.8	Done	
OCTANE	RON+MON/2	89.2000	89.2	Done	

Figure 8. LIMS database with on specification EUROBOB_S, Octanes shown.

The octane rating of a gasoline can be thought of as a measure of the gasolines resistance to detonation or ‘engine knocking’. High performance engines will typically require a higher octane fuel due to the fact they have higher compression ratios and thus detonation within the engine is more easily attained. Figure 8 shows the site LIMS with neat and corrected values shown for EUROBOB_S grade gasoline.

10.1.2 Use of the Transept IV Interferometer

To produce the required interferogram's and spectra via the laboratory test equipment the following is a detailed explanation of each step the technicians must take to produce the desired results. An interpretation of the interferometer used in the site FTIR analyser can be seen in Figure 9.

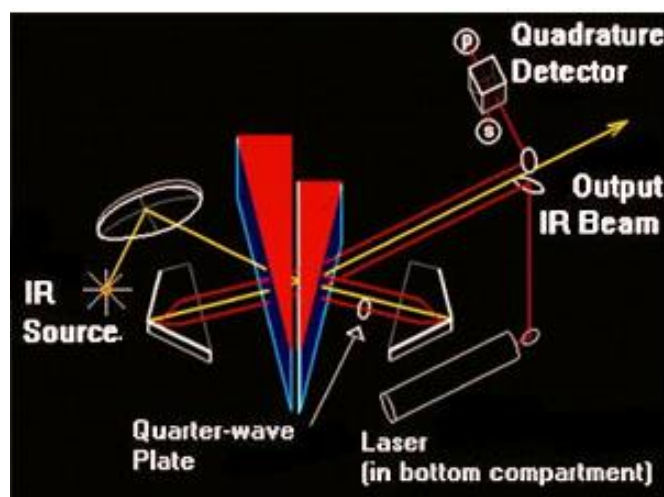


Figure 9. Site FTIR 'Transept IV' Interferometer (AIT, 2012)

Preparation of the sample is very important. A background spectrum needs to be collected, using the same method as shown above the background sample is used to account for source faults, detector faults, interferometer errors, and ambient water and carbon dioxide. As the background is taken directly before the sample is introduced to the cell the above sources of variability should be the same and thus, provide a resultant background which is then used as a substitute within the final calculations of sample spectra to ensure the resultant spectra is only showing information about the sample analysed.

10.1.3 Laboratory Testing of BOB Specification Gasoline

Full procedure available in appendix 15.2

5. Procedure

5.1. All tanks that require ethanol hand blends in addition to the base blend will be clearly marked on the ROP by scheduling.

5.2. Testing of the base blend and hand blend should be performed as per the nominated specification and the lab BOB spec gasoline handblend test list.

LAB/PRO/003 A1 Issue 2.3 Page 2 of 2 Printed on 31/10/2017 **Uncontrolled when printed**

5.3. On receipt of the tank samples the density should be carried out first to confirm it is uniform, once this is done the ethanol hand blend should be prepared using denatured ethanol

(stored in CSR) take care that the ethanol and base blend are at the same temperature prior to making the volumetric blend.

5.4. Testing of both the base blend and hand blend should be commenced at the same time with equal priority. Any difficulty in progressing this work due to high workload should be discussed with scheduling.

5.5. All calculations required will be done outside of StarLIMS (V/L, driveability, API for Colonial and VLI for European) and can be found via the laboratory intranet page or V:\laboratory\reference\calculations\Mogas

5.6. If required the predictive models are available via the scheduling intranet page in the *Gasoline Spreadsheets* folder

5.7. Each completed predictive model spreadsheet should be saved in V:\Laboratory\Public\Predictive model spreadsheet. And emailed to GMfg-PEM Scheduling & Quality.

5.8. Where testing of the hand blend is carried out the batch should be released based on hand blend results, hard copy specification should always be referred to prior to release.

5.9. The CoA for the ethanol hand blend tank should display a full set of results for base blend with no specs and all results for the hand blend tests that are included in the *BOB spec gasoline handblend test list with specs, all non handblend batches will only have base blend results and therefore no specification visible on the CoA*

5.9.1. If testing a batch that does not require hand blend testing do not delete the ethanol tag in LIMS as it may cause problem if later requested to perform any hand blend testing to check predicted qualities.

5.9.2. Any tests for the handblend that are not requested on the ROP should be left blank in LIMS, do not delete or enter typical type test values.

(Manson. 2012)

10.1.4 Preparing Ethanol and gasoline Blendstock Hand Blends

Full procedure available in appendix 15.1

5. Procedure

Note: All glassware to be used in the hand blend must be grade A and should be sealed to help prevent the formation of condensation when being chilled.

5.1. Chill apparatus, gasoline blendstock samples and denatured fuel ethanol to be used in blending to between 0°C & 4°C.

5.2. Determine the ethanol percentage required in the final blend, this information is supplied by scheduling and is stated on the ROP.

5.3. Determine how much sample is required to complete all of the required testing and have enough for retention purposes. A minimum of 1.5 litres is required for retention.

5.4. Use equation 6.1 below to calculate the amount of ethanol to be blended.

5.5. Perform the following steps as efficiently as possible so as to minimise temperature increase and the loss of light ends.

5.5.1. Measure the volume of denatured ethanol required in a suitable volumetric measuring device.

5.5.2. Add the denatured ethanol to the volumetric flask and bring up to the volume with gasoline blend stock.

5.5.3. Thoroughly mix the blend but **do not** shake vigorously as this will result in light end loss and will affect vapour pressure results.

6. Calculations

6.1. Volume of denatured ethanol for blend

$$V_{de} = [\%E/100] * V_b$$

V_{de} = Volume of denatured ethanol (ml)

$\%E$ = final percentage of denatured ethanol required in final blend

V_b = Target volume of final blend (ml) (e.g. amount of sample required for testing and retention)

(Davies. 2014)

10.1.5 Spectra capture via laboratory analyser

Using the FTIR analyser and automatic sampler, stationed within a fume extraction hood in the engine laboratory, shown in figure 10, a number of prepared samples are placed in numbered holders within the automatic sample apparatus. The LIMS code for each sample is entered into the corresponding numbers cell within the sample software (SpectraQ).

A background sample is run – when completed the analyser cleans the cell with cyclohexane and purges the cell using nitrogen for an extended period to ensure the cell is dry. The IR radiation source is passed through the sample cell providing a background spectrum which as

stated previously can then be used as a substitute during real samples. The background has some threshold values it must be between, if the results are good the background is used, if not an error is displayed and this will need to be rectified before analysis can be performed.

A validation sample is run on the analyser – toluene is used for this test and an arbitrary figure of 1000 is used as a base line validation for toluene. Once the validation sample is complete the computer validates the result against the 1000 specification and as long as the result is between 900 and 1100 the analyser is validated and can now be used for full analysis.



Figure 10. Laboratory automatic sampler and FTIR spectrometer in fume hood.

Once the analyser passes its validation, then the software is ready to have the sample numbers entered for the specific samples and run the collection. Collection takes around five to ten minutes per sample and a spectra is produced for each sample which is successfully analysed.

To use the hardware efficiently multiple retained samples are gathered and run at the same time, a typical spectrum output is shown in figure 11. This spectrum output requires scrutinising and any erroneous samples can be removed from the sample set at this time.

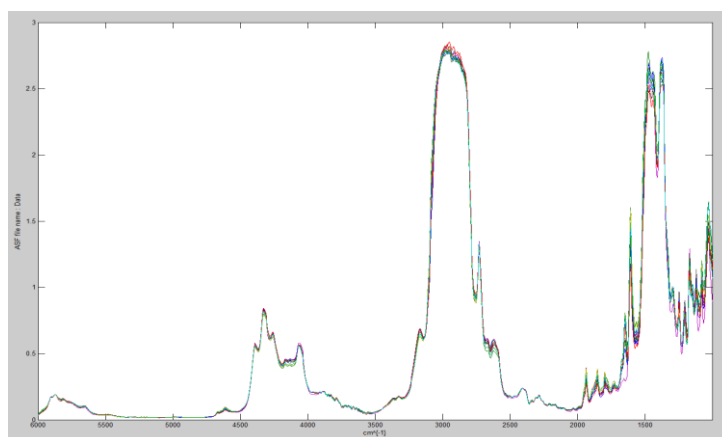


Figure 11. Sample spectrum for EUROBOB_S

Only some regions of the spectrum shown above have data relevant to the analysis which is required so the system allows for the addition of regions to the spectrum which do require analysis, the site values for these regions are shown in figure 12.

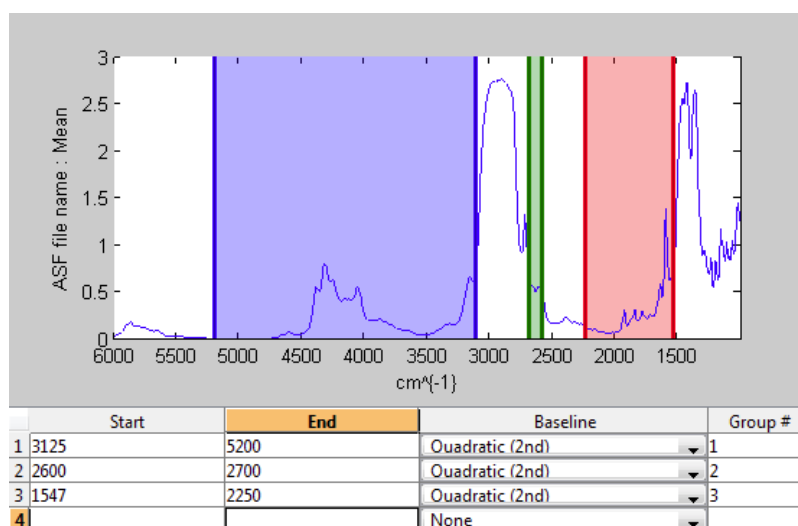


Figure 12. Relevant regions of spectrum analysed

It is only at this point that the software will allow the user to build a model. At this point the principal component number can be selected, this is the number of principal components the software will use to reach a solution while analysing the data. After some time working with this hardware and software on gasoline blends this number normally starts around six or eight. There are three main objectives of the topology review carried out at this point which need to be explained, namely; R^2 , RMSEC and RMSECV.

R^2 The multiple correlation coefficient – this value is informing the user how good the data presented fits the ideal of 1. When carrying out the topology review of the data ideally moving this value towards 1 will gain better final results.

RMSEC Root Mean Squared Error of Calibration – this value shows the accuracy between the 'model values' and the laboratory values being analysed. The lower this figure the better ideally driving this figure towards 0 yields better results.

RMSECV Root Mean Squared Error of Cross Validation – this is again the accuracy between the ‘model values’ and the laboratory values after cross validation has been applied to the data being analysed. Again driving the value towards 0 yields better results.

Once the initial model has been populated with spectra results, three trends are displayed, each presenting relevant information on the data output by the spectrometer. Figure 13 shows the first trend of Hotelling (T^2) against Q Residuals (in percentage), and within this trend the dashed lines are the 95 percent confidence limits for the two variables. Samples outside these values should be scrutinised closely as they are signifying large differences between themselves and the rest of the spectra. Each dot on the trend represents one spectra including existing and new spectra. Values circled (in red) in figure 13 as stated should be scrutinised and could ultimately be removed to improve the overall model.

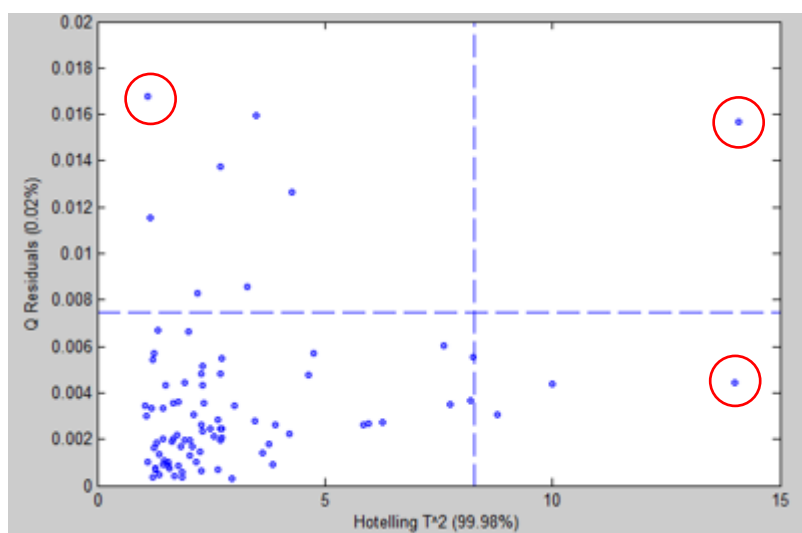


Figure 13. Spectrum modelling hotelling t^2 against Q residuals.

Figure 14 shows the second trend of Leverage against Y studentised residual, this trend is also useful while analysing the data, this trend plots leverage against the lack of fit of a value within the sample. Leverage is shown from left to right so values to the right of the dashed vertical line are having a much larger influence on the model than the cluster on the left (circled in green). Values a distance away from the horizontal mean at zero here may also be having a detrimental effect on the final model (circled in blue).

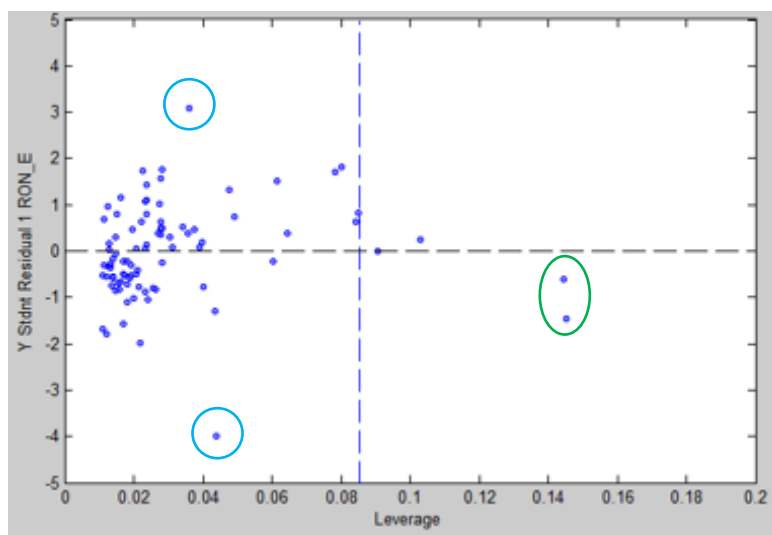


Figure 14. Spectrum modelling Leverage against Y Studentised residual

The final trend used at this time normally shows the most relevant and understandable data available. This trend plots the predicted values against the measured values, values in this trend are what the spectrometer predicted against what the engines actually gave as results when the sample was analysed. Figure 15 shows the trend and by removing outlying spectra the aim is to move the red line as close over the green line as possible. When selecting samples on any trend they will highlight pink on all trends enabling for swift verification if a suspect spectra on one trend is also an outlier on the others.

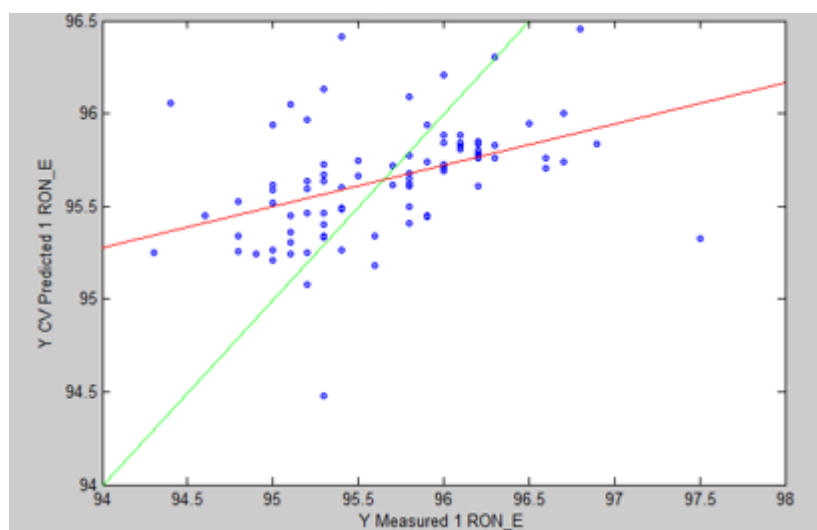


Figure 15. Spectrum modelling Y predicted against Y measured.

Once a number of spectra have been removed the three objectives (R^2 , RMSEC and RMSECV) can be reviewed and if improvements have been seen the model can be rebuilt and the number of principal components checked and the above cycle repeated until a reliable model has been established.

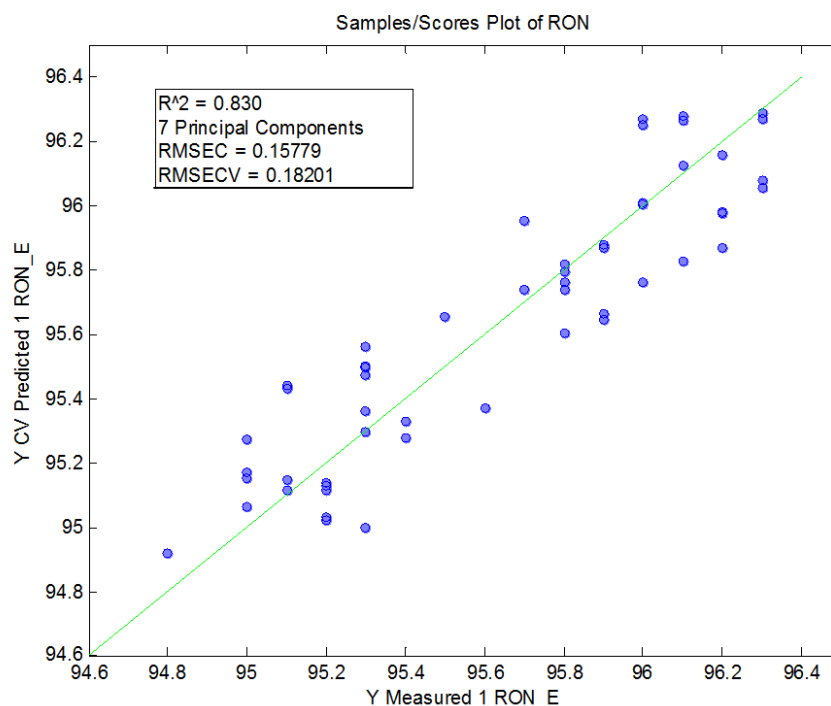


Figure 16. Final 2014 model of RON for EUROBOB_S

Figure 16 shows the existing model which is currently being used online at site, is contains around 50 sample spectra from a sample size of around eighty. Figure 17 shows the 2018 proposed model of RON for EUROBOB_S (All other models can be viewed in Appendix 15.6). This model includes around twenty to thirty more spectra than the 2014 model. It is also working across a much wider range than the previous model, while the 2014 model had spectra ranging from 94.8 to 96.3 RON, the 2018 model is now working between 94.3 and 96.7. What this means is any online RON values within this range can now be used to move the blend to an on specification range whereas in 2014 anything outside the original range would have forced the optimiser to an infeasible state.

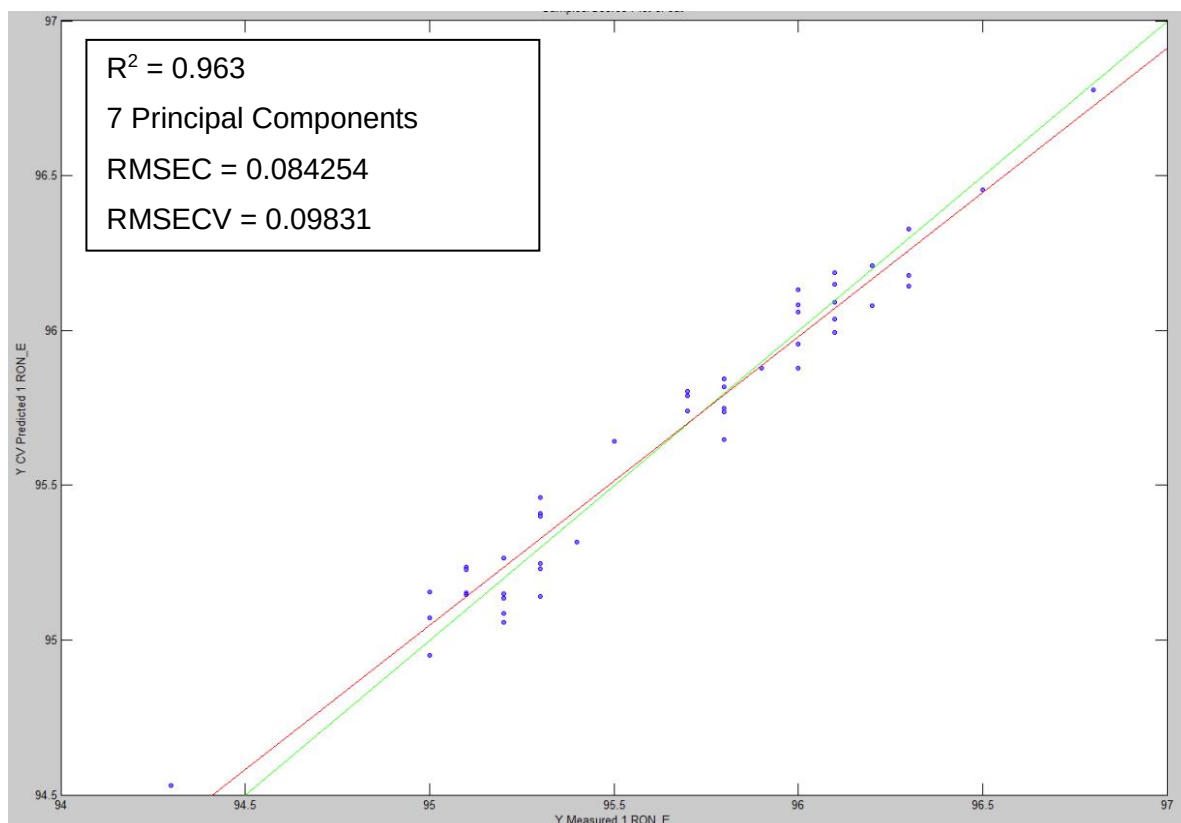


Figure 17. Proposed 2018 model of RON for EUROBOB_S

10.2 Experiment 1

Once the first set of models had been created using the software, a set of laboratory tests were devised to ascertain if the improvements observed to the R^2 , RMSEC and RMSECV had made a difference to the overall results received for a set of retained samples, which results were readily available for. It was decided for the sake of the repeatability of the experiments one laboratory technician would make up all the base samples and 'spiked' samples to eliminate human error from the experiments before they can be introduced, but the CSE Specialist is to be in attendance to run the software. Each sample bottle used in the laboratory FTIR holds a volume of 40ml so 50ml of sample is measured into a graduated cylinder and for the first experiment all samples were run neat with no Platformate. A small amount of the gasoline is used to clean the inside of the sample bottle and discarded. The sample is then poured into the sample bottle and a permeable cap made of PTFE and silicone is placed on the sample bottle. This process is repeated for all samples.

Table 3 below is the first experiment carried out with the old and new models and will be used as the basis for explaining how the following tables can be interpreted. The LIMS ID comes directly from the site LIMS database, from this LIMS number the engine results for RON and MON so 96.00 and 85.40 respectively are also collected. The FTIR Model column shows which model was used for that specific row of results. The FTIR column for both RON and MON is the new data results supplied by the FTIR while running the experiment. The Delta column is the difference between the FTIR and Engine results, for this column conditional formatting was included to help identify substantial changes to the results, the conditional formatting cut-off point was taken as the site capability KPI value shown in chapter 9.3 – (0.29ON) any value outside this capability would send the cell **Red** any value within this capability will change the cell **Green**.

Table 4 Neat Gasoline Sample #1

Neat Gasoline Sample #1		RON			MON		
LIMS ID	FTIR Model	FTIR	Engine	Delta	FTIR	Engine	Delta
610671 #1	EUROBOB_S OLD	96.00	96.00	0.00	85.61	85.40	0.21
610671 #2	EUROBOB_S OLD	96.01	96.00	0.00	85.61	85.40	0.21
610671 #1	EUROBOB_S NEW	95.69	96.00	-0.31	85.60	85.40	0.20
610671 #2	EUROBOB_S NEW	95.62	96.00	-0.38	85.35	85.40	-0.05

10.2.1 Neat Sample #1

Table 4 clearly shows that while the new model for MON has only changed by 0.01ON for sample #1 a step change towards the engine result is seen in sample #2. While this could be seen as a positive for the new model the results of the RON samples are somewhat more problematic. With a FTIR value from the old model close to the engine results, the new RON model was outside the site capability in both cases. At this point the RON model does not look to be analysing the samples to the same accuracy as the old model.

Table 5 Neat Gasoline Sample #2

Neat Gasoline Sample #2		RON			MON		
LIMS ID	FTIR Model	FTIR	Engine	Delta	FTIR	Engine	Delta
611325 #1	EUROBOB_S OLD	95.76	95.40	0.36	85.19	85.20	-0.01
611325 #2	EUROBOB_S OLD	95.80	95.40	0.40	85.24	85.20	0.04
611325 #1	EUROBOB_S NEW	95.55	95.40	0.15	85.08	85.20	-0.12
611325 #2	EUROBOB_S NEW	95.55	95.40	0.15	85.07	85.20	-0.13

10.2.2 Neat Sample #2

Table 5 shows an improvement to the RON model with no changes made to the model itself. RON delta between the new model and the engine are showing an improvement of accuracy to the old model which had results well outside the site capability, this sample has also given better repeatability with both results giving a delta of 0.15ON well within the site capability. MON in this case has shifted away from the engine result but is still well within the site capability and in this case, being below the engine result would make the final engine result closer to the final specification and minimise giveaway.

Table 6 Neat Gasoline Sample #3

Neat Gasoline Sample #3		RON			MON		
LIMS ID	FTIR Model	FTIR	Engine	Delta	FTIR	Engine	Delta
610317 #1	EUROBOB_S OLD	96.34	96.20	0.19	85.02	85.20	-0.18
610317 #2	EUROBOB_S OLD	96.40	96.20	0.19	85.04	85.20	-0.17
610317 #1	EUROBOB_S NEW	95.96	96.20	-0.24	84.95	85.20	-0.25
610317 #2	EUROBOB_S NEW	95.94	96.20	-0.26	84.93	85.20	-0.27

10.2.3 Neat Sample #3

Table 6 shows more variability in the RON model as seen in the first sample but all results are within the site capability and with the new model they are below the engine result so again will assist in returning a final engine result for the sample closer to the specification without allowing giveaway. MON in this case has also shifted away from the engine result but is still within the site capability.

Table 7 Neat Gasoline Sample #4

Neat Gasoline Sample #4		RON			MON		
LIMS ID	FTIR Model	FTIR	Engine	Delta	FTIR	Engine	Delta
611848 #1	EUROBOB_S OLD	95.44	95.20	0.24	85.40	85.30	0.10
611848 #1	EUROBOB_S NEW	95.44	95.20	0.24	85.06	85.30	-0.24

10.2.4 Neat Sample #4

Table 7 shows a solid RON model with no delta between the old and new models but still closer to the maximum site capability. MON in this case has also shifted away from the engine result but is still within the site capability.

With a degree of variability with the new model from this point the decision was made to repeat the above experiments with 5 and 10 percent Platformate included. As the model will never be used neat the above results give a marker for the new model but the next set of results should demonstrate the capability of the new model over the old.

10.3 Experiment 2

Once the first experiment was finished the second experiment is to add Platformate. Ethanol is never introduced to the laboratory FTIR analyser, due to its water soluble nature, the boost in octane number received when ethanol is introduced to the gasoline is inferred. Platformate will be used as a boosting agent to 'spike' the gasoline to determine if the new models would provide results closer to the engine results than previously. With the introduction of the Platformate again each sample bottle used in the FTIR holds a volume of 40ml so 50ml of sample is measured into a graduated cylinder, and 5ml of Platformate (10 percent) is added to the cylinder the mixture is stirred, a small amount used to clean the inside of the sample bottle and discarded. The sample is then poured into the sample bottle and a permeable cap placed on the sample bottle. This process is repeated for all samples being tested. During this testing phase 5 percent 'spiked' gasoline and 10 percent 'spiked' gasoline were tested. As can be seen from the LIMS numbers in these sample where possible the same gasoline samples were used as in experiment 1.

Table 8 Spiked Gasoline Sample #1

Spiked Gasoline Sample #1			RON			MON		
LIMS ID	FTIR Model	Spike %	FTIR	Engine	Delta	FTIR	Engine	Delta
610671 #1	EUROBOB_S OLD	5	96.70	96.13	0.58	85.45	85.53	-0.08
610671 #2	EUROBOB_S OLD	5	97.06	96.13	0.93	85.54	85.53	0.01
610671 #1	EUROBOB_S OLD	10	96.88	96.25	0.63	85.50	85.66	-0.17
610671 #2	EUROBOB_S OLD	10	97.24	96.25	0.99	85.58	85.66	-0.08
610671 #1	EUROBOB_S NEW	5	95.79	96.13	-0.33	85.64	85.53	0.11
610671 #2	EUROBOB_S NEW	5	95.78	96.13	-0.34	85.65	85.53	0.12
610671 #1	EUROBOB_S NEW	10	95.86	96.25	-0.39	85.71	85.66	0.05
610671 #2	EUROBOB_S NEW	10	95.88	96.25	-0.38	85.76	85.66	0.10

10.3.1 Spiked Sample #1

Table 8 shows an improvement over the previous RON model which was almost a whole Octane Number high when compared to the engine results. Although the results are still outside the site capability values the accuracy and repeatability is improving. MON in this case has also shifted away from the engine result but is still within the site capability.

Table 9 Spiked Gasoline Sample #2

Spiked Gasoline Sample #2			RON			MON		
LIMS ID	FTIR Model	Spike %	FTIR	Engine	Delta	FTIR	Engine	Delta
611325 #1	EUROBOB_S OLD	5	95.99	95.56	0.44	85.28	85.34	-0.06
611325 #2	EUROBOB_S OLD	5	96.35	95.56	0.79	85.36	85.34	0.02
611325 #1	EUROBOB_S OLD	10	96.17	95.71	0.46	85.32	85.48	-0.16
611325 #2	EUROBOB_S OLD	10	96.52	95.71	0.81	85.41	85.48	-0.07
611325 #1	EUROBOB_S NEW	5	95.67	95.56	0.11	85.23	85.34	-0.11
611325 #2	EUROBOB_S NEW	5	95.66	95.56	0.10	85.24	85.34	-0.10
611325 #1	EUROBOB_S NEW	10	95.68	95.71	-0.03	85.23	85.48	-0.25
611325 #2	EUROBOB_S NEW	10	95.71	95.71	0.00	85.28	85.48	-0.20

10.3.2 Spiked Sample #2

Table 9 shows a vast improvement over the previous RON model again with much reduced variability and all results within the site capability. MON in this case has also shifted away from the engine result but is still within the site capability.

Table 10 Spiked Gasoline Sample #3

Spiked Gasoline Sample #3			RON			MON		
LIMS ID	FTIR Model	Spike %	FTIR	Engine	Delta	FTIR	Engine	Delta
611848 #1	EUROBOB_S OLD	10	95.93	95.53	0.39	85.54	85.57	-0.03
611848 #2	EUROBOB_S NEW	10	95.67	95.53	0.14	85.35	85.57	-0.22

10.3.3 Spiked Sample #3

Table 10 again shows an improvement over the previous RON model bringing the result well within the site capability, due to the lack of retained sample only a 10 percent sample could be run for this test. MON in this case has again shifted away from the engine result but is still within the site capability.

10.4 Management of Change

At Pembroke all changes must be tracked and risk assessed by a team of competent persons, led by an approved chairperson, the CSE specialist in this case. Once the above results had been presented to the blend focus team and had been accepted a Management of Change (MOC) was conducted and can be seen in the Appendix 15.4, the team will identify a hazard introduced by this change and its consequence – for a risk that can have multiple consequences the most dangerous consequence must be selected (safety, environment, community) these risks would all come above a business risk which would just be a loss of finance. The team will then discuss the circumstances this hazard could be seen, enter any existing control measures then risk rank the hazard using the Valero risk matrix shown in figure 18. During this discussion the likelihood of this hazard is understood and with this and the consequence, a risk level is obtained. The team will then enter all recommendations that are practical to execute and each of these recommendations should be able to move the risk from a higher likelihood to a lower likelihood. The Valero Energy Ltd Risk Matrix states, all level 1 to 5 risks are unacceptable and recommendations will have to be enforced regardless of price. Tolerable Risks (TR) should be discussed further and best efforts should be made to move the risk level to As Low As Reasonably Practical (ALARP). If this risk can be demonstrated to have dropped to ALARP a tolerable risk is ok. Where practical all risks should be reduced to Broadly Acceptable (BA).

For this MOC the team comprised of the Control Systems Specialist (myself), P&E team member, Laboratory Supervisor and Engine Laboratory technician, and the area operations advisor.

Valero Risk Matrix - Modified for Pembroke.				VALERO								
Business	Environment	Consequence	Safety									
>\$100 Million	Catastrophic - Serious contamination of ground water or water course, extensive loss of aquatic life.	Public Evacuation or National Media Coverage	>10 Fatalities On Site or Multiple Fatalities Off Site	VI	TR	Level 1	Level 2	Level 3	Level 4	Level 4	Level 5	
>\$10MM to \$100MM	Major - Serious toxic effect on beneficial or protected species, significant fish kill over a five mile range.	Public Evacuation or County Media Coverage	2 to 10 Fatalities On Site or One Fatality Off Site	V	TR	TR	Level 1	Level 2	Level 3	Level 3	Level 4	
>\$1MM to \$10MM	Severe - Hazardous material into water course with half mile effect, e.g. Visible Fish Kill	Shelter in Place or County Media Coverage	Permanent Disabling Injury (e.g. Amputation) to Single Fatality	IV	BA	TR	TR	Level 1	Level 2	Level 2	Level 3	
>\$100K to \$1 MM	Significant - Strong or offensive odours or noise, major breach of permitted emissions	Shelter in Place or Local Area Media Coverage	Serious Injury to Permanent Injury (e.g. Burn)	III	BA	BA	TR	TR	Level 1	Level 1	Level 2	
>\$10K to \$100K	Noticeable - Nuisance off site, discernible odours, minor breach of permit conditions	Community Warning or Local Media Coverage	Recordable to Lost Time	II	BA	BA	BA	BA	TR	TR	Level 1	
<\$10K	Minor - Nuisance On site only, No off site effects	No to minor impact to people or No Media Coverage	Minor to First Aid	I	BA	BA	BA	BA	BA	BA	TR	
Likelihood D					AAA	AA	A	B	C	D	E	
Qualitative description					Rare - equivalent to being killed by a lightning strike.	Remote, has occurred once or twice in the industry	Unlikely that the event will occur at this facility.	Conditions may allow the event to occur within industry using similar technology	Conditions may allow the event to occur at this facility during its lifetime	Likely to occur at this facility once every 10 years	Highly to occur	
Scenario frequency per annum					10-7 to 10-6	10-6 to 10-5	10-5 to 10-4	10-4 to 10-3	10-3 to 10-2	10-2 to 10-1	10-1 to 1	

Legend:

Level 2, 3, 4 and 5 Unacceptable Risk.
Must be reduced regardless of cost - Short term, interim risk reduction required.
Long term risk reduction plan must be developed and implemented, to reduce the risk.
If the consequence is "IV" or higher and the risk cannot be reduced to "TR" or at least "Level 1" due to the cost of controls being disproportionate, then the activity must be abandoned.

Level 1 - Undesirable risk.
If the consequence is "IV" or higher and the risk cannot be reduced to at least "TR" due to the cost of controls being disproportionate then the activity can only be continued with appropriate manager sign off at Level One authority providing a robust ALARP demonstration is made.
This may involve a quantitative risk assessment e.g. LoPA / QRA with a CBA - Contact PSM personnel for advice.
If the consequences are between "I and III" then a qualitative risk assessment can be used for ALARP demonstration, e.g. Team review - What more can we do? Why aren't we doing it?

TR - Risk is tolerable if ALARP
Further control measures must be investigated and implemented if reasonable to do so. If the consequences are "IV" or higher an ALARP demonstration may be required to determine what is reasonable. Contact PSM personnel for advice.
If the consequences are between "I and III" then a qualitative risk assessment can be used for ALARP demonstration, e.g. Team review - What more can we do? Why aren't we doing it?

BA - Broadly Acceptable
The risk is acceptable if all controls are in place and recommended good practice is followed.

Figure 18. Valero Risk Matrix (Valero Energy Ltd, 2016)

As this change will be a permanent risk assessment many of the recommendations included have been seen as temporary safeguards not permanent and as they will only be temporary safeguards they do not move the likelihood of the risk down due to the fact that once the test has been run on two to three online blends and proved to work the temporary safeguards will be relaxed so the risk will remain. As these risks are already at TR and all practical control measures are in place for the current blend models the decision was made to move forward with the uploading of the new models to the online FTIR analysers. During this MOC the decision was also made to attempt to capture all steps in a single procedure which could be used as a tracking document in future model upgrades.

10.4.1 Human Factors within the management of change system

With each MOC raised at Pembroke a section of the risk assessment must revolve around human factors. 'Human factors refer to environmental, organisational and job factors, and human and individual characteristics which influence behaviour at work in a way which can affect health and safety' (HSE, 2009). Using these three functions the risks for each can be

assessed with a view to eliminating human error. There are different types of human failure to consider while carrying out a MOC, errors and violations.

The HSE (2009) states a human error occurs as a result of an action or decision which was not intended, this results in a deviation from acceptable limits or undesirable outcomes.

The HSE (2009) also states a human violation is a deliberate deviation from a rule or procedure.

Assessing human errors. A skill based error would be assessed against two failures a slip or a lapse. A slip is a failure while carrying out the actions of a task. For example operating the wrong switch or copying numeric data incorrectly. A lapse causes the operator to forget which steps of a procedure have been carried out. For example opening a valve, being distracted by a question asked over the radio and closing the valve again.

Mistakes can also be sectioned into two failures rule-based mistakes or knowledge based mistakes. A rule based mistake occurs when a familiar task is being carried out without the correct procedure available to assist the operator. A simple sample collection can provide an untestable sample if the operator forgets to check a good pressure and flow are present within the MSCS at the start of collection. A knowledge based mistake can occur if no or inadequate training has been provided to an operator who is now carrying out a task alone. Inexperience or lack of information can mean errors occur more frequently.

Assessing human violations. A routine violation can occurs when the operator believes the rules are too restrictive on the task being carried out or a saving in time or energy can be seen. A situational violation can occur when pressure, lack of time, inadequate manning or equipment failure are forcing the operator to make bad decisions. For example the need to start blending a tank very near shift change could mean the operators do not fully carry out all required checks on equipment or recipe and unfound faults cause a failure. Exceptional violations occur very rarely and normally when other factors have already gone wrong and the benefits of violating a rule outweigh the risk.

These errors and violations need to be assessed during a MOC to help eliminate as many human factors as possible before any new system is put into production at Pembroke. One major human factor identified during this MOC was the requirement to produce a procedure of the step required to update or create a new set of models for a grade of gasoline. By creating a procedure many of the slips could be eliminated as each step to be carried out would be written for the operator carrying out the step. Lapses can still occur even with the correct procedure in place but eliminating distractions can help alleviate the pressure the operator might face during the procedure, planning a week of the laboratory technician's time to work

only on updating and testing models and scheduling this time in to the calendar mean the technician can stay focused on this task while other technicians run the engine laboratory without issue. Again allowing the laboratory technician to focus and use the correct procedure for preparing samples for testing in the FTIR analyser can reduce rule based mistakes. Ensuring multiple laboratory technicians have been trained in the use of the FTIR analyser and have suitable time to use the analyser each time it is required will help eliminate the knowledge based mistakes, and also positively reinforcing the technicians to ask questions if they are not sure of the next steps required while using the hardware or software. Mitigating a routine violation can be achieved by ensuring each operator understands the importance of the task being carried out to the bigger undertaking being achieved. If the operator understands the sample being taken from the MSCS needs to represent the recipe being blended one hour in to a blend as the ship is waiting for the on specification blend, the operator will be more likely to take that sample at the one hour mark exactly. Situational violations can be reduced by informing the operators that no blend should be started within two hours of shift change. Preparations can be made to the field equipment and the recipe can be checked for errors from the P&E department but starting the blend should be left to the next shift who have twelve hours to observe problems that may occur. Exceptional violations can be reduced naturally if all other step above have been followed but training the operators to ensure they can safely shutdown the blend system should a problem occur is better than allowing the operations team to fight a problem and create a bigger risk by believing they are helping.

10.5 Upload of models to online FTIR analysers

All individuals with actions from the MOC must carry out these actions before the change can be performed. Each action needs to be entered into the MOC system with the responsible person named. Once the action is completed that individual can enter the system and sign off the action. Once all actions are completed the change can be made to the online analyser system. Each new model needs to be checked against the existing online model and the filenames matched up. The created table (TBL) files require the same names as the existing TBL files as at the start of each new blend the system sends the grade name to the analyser and it is from this the analyser selects which models to use.

For EUROBOB_S gasoline table 11 shows the model TBL files are currently used in the online analysers.

Table 11 Existing and new model names for EUROBOB_S grade gasoline

SUM_ARO_5E.TBL	Summer aromatic model with 5% Ethanol
ALL_BEN_5E.TBL (SUM_BEN_5E.TBL)	Benzene model with 5% Ethanol, included in ALL blends analysing benzene, this will be modified to summer only.
SUM_E70_E5.TBL	Summer evaporation point at 70°C model with 5% Ethanol
SUM_E100_E5.TBL	Summer evaporation point at 100°C model with 5% Ethanol
SUM_E150_E5.TBL	Summer evaporation point at 150°C model with 5% Ethanol
SUM_FBP_E5.TBL	Summer final boiling point with 5% Ethanol
SUM_MON_E5.TBL	Summer MON with 5% Ethanol
SUM_OLE_E5.TBL	Summer Olefin model with 5% Ethanol
SUM_ROM_E5.TBL	Summer RON model with 5% Ethanol

The new models are renamed on the laboratory system and moved onto a virus checked memory stick (as these analysers have access to the process control network testing is mandatory). The models can then be moved to the analyser house. Backups of the existing online models are taken and moved to the memory stick to ensure a back out plan is available should any problems with the new models are seen. The new models are copied into the two online analysers, ensuring when copied each one gives a warning that it is replacing an existing model. Once this is done a EUROBOB_S blend can be started from the Blend optimisation system.

Table 12 Extract from April 2018 Blend Performance Review

TANK	Blend Release	Blend End Date/Time	bbls Blended	Reblend	Grade (Product ID)	% Closed Loop	Avg % Recipe Dev.	Feasible at 1st sample	Feasible at final tank	Per blend saving
20T817	18G104	02-Apr-18 05:37	105040		RBOBUNLV2	100%	1%	Yes	Yes	\$ 9,619.73
20T816	18G105	03-Apr-18 02:00	105039		RBOBUNLV2	100%	2%	Yes	Yes	\$ 72,533.07
20D111	18G106	03-Apr-18 18:54	102354		RBOBUNLV2	100%	1%	No	Yes	Correction Passed
20D117	18G107	04-Apr-18 12:23	108242		EUROBOB-S	99%	3%	No	Yes	Correction Passed
20T817	18G109	05-Apr-18 07:54	125945		RBOBUNLV2	100%	3%	Yes	Yes	\$ 123,739.47
20D113	18G110	05-Apr-18 17:59	59650		EUROBOB-S	59%	1%	Yes	Yes	\$ 19,912.87
20T816	18G114	06-Apr-18 09:41	101990		RBOBUNLV2	100%	3%	Yes	Yes	\$ 121,366.66
20D111	18G115	07-Apr-18 06:38	85730		RBOBUNLV2	99%	3%	Yes	Yes	\$ 18,437.94
BERTH 2	18G113	07-Apr-18 21:26	40700		RBOBPREV2	93%	0%	Yes	Yes	\$ 2,131.42
20T817	18G116	08-Apr-18 07:30	75504		RBOBUNLV2	100%	2%	No	Yes	Correction Passed
20T816	18G117	08-Apr-18 19:38	98948		RBOBUNLV2	100%	2%	Yes	Yes	\$ 100,788.76
20D113	18G120A	09-Apr-18 10:52	9450		95EN228-S	0%	0%	Yes	No	\$ -
20D110	18G118A	09-Apr-18 23:20	86485		EUROBOB-S	0%	0%	Yes	No	\$ -
20D113	18G123	10-Apr-18 18:31	8825		95EN228-S	0%	0%	Yes	No	\$ -
BERTH 1	18G120	11-Apr-18 14:00	77345		EURO_SUM	94%	2%	No	Yes	Correction Passed
20D113	18G123R	11-Apr-18 16:57	10700		95EN228-S	0%	0%	Yes	No	\$ -
20T816	18G124	12-Apr-18 02:57	50007		CAN-CBOB-60K	0%	0%	Yes	No	\$ -
20D111	18G126	13-Apr-18 04:29	98933		RBOBUNLV2	100%	3%	Yes	Yes	\$ 73,862.81
20D110	18G128	13-Apr-18 11:21	27448		EUROBOB-S	0%	0%	Yes	No	\$ -
BERTH 8	18G126A	13-Apr-18 19:34	41279		EURO_SUM	97%	4%	No	No	Correction Failed
20D110	18G128A	14-Apr-18 05:56	65031		EUROBOB-S	100%	3%	No	Yes	Correction Passed

Shown in table 12 is the early extract from the monthly blend performance report produced at Pembroke and published to the corporate SME in San Antonio. The new models were installed in the online FTIR analysers on the third of April 2018, this task was carried out at this time as summer grade gasoline production at site commences around the sixth of April every year.

As highlighted in table 12 the gasoline blender has performed four EUROBOB_S gasoline blends so far this month, the first to tank 20D117 was able to move an off specification blend at first sample to within the specification range before blend completion. As shown in section 9.4 this is seen as a positive result for the blend optimiser since the recipe run in ratio would have produced off specification gasoline, so a re-blend has been prevented by the optimiser and the FTIR analyser.

The second blend to tank 20D110 started with an on specification blend which was then fully optimised. During this blend there was an issue with field hardware which resulted in the blend being placed in ratio around half way through the blend, even with this low percentage of optimiser usage the saving on the blend for a deviation from initial recipe of 1 percent was still \$19,912.87 so the models seem to be able to control the properties within the blend well. At this stage the decision was made to continue using the models and analysing the feedback from operations personnel and the results seen on the system.

The third EUROBOB_S recipe blended this month did not use the optimiser. Feedback from operations has not been given as to why this blend was not optimised and this blend was the first of the EUROBOB_S blends to finish off specification, an opportunity was missed here to optimise a large cargo of EUROBOB_S at a time when this would have been beneficial to this project but also to reduce the chances of blending off specification gasoline.

The final two blends highlighted in this table, blended to tank 20D110 show another lost profit opportunity for the optimiser. This blend carried out on a day when the blend focus team was not available to monitor the blend, it was not optimised and again resulted in an off specification final blend, but the re-blend of this tank carried out on the next day was optimised and resulted in the optimiser and FTIR analysers being able to manipulate the blend from an off specification blend to an on specification blend, again helping to prove the models are working correctly.

11. Timeframe

Table 13 EUROBOB_S model upgrade timeframe

2017	Sep 4	Sep 12	Sep 20	Sep 28	Oct 6	Oct 14	Oct 22	Oct 30	Nov 7	Nov 15	Nov 23	Dec 1	Dec 9	Dec 17	Dec 25
Collect samples															
Test existing model															
Run new and samples through Laboratory FTIR															
Reconfigure existing EUROBOB_S model															
Site change freeze															
2018	Jan 2	Jan 10	Jan 18	Jan 26	Feb 3	Feb 11	Feb 19	Feb 27	Mar 7	Mar 15	Mar 23	Mar 31	Apr 8	Apr 16	Apr 24
Site change freeze															
Reconfigure existing EUROBOB_S model															
Test new model with neat gasoline retained samples															
Test new model with spiked gasoline retained samples															
Present new model to Blend Focus Team															
Trail new models in online system															
Modify online models															
Move onto next Grade															

12. Conclusion

During this project there have been many items found which will aid in the successful continuation of this project at Pembroke site.

The need to identify problematic grades of gasoline early so the laboratory staff can start retaining samples for use when that grade needs improving.

The importance of providing time in the laboratory technicians schedule to focus on this task without the distraction of normal engine lab routine duties. The need to have more than one laboratory technician trained in the used of the FTIR analyser and the modelling software, and the need to have two sets of eyes on the modelling process and topology review while it is being carried out to ensure the correct resulting spectra are being used or discarded as required, in this case the laboratory technician and the CSE specialist. The significance of using the procedures provided when making neat and 'spiked' hand blends for testing.

During this project it was also reiterated to the operations personnel responsible for taking samples from the MSCS that ensuring good pressure and positive flow are detected within the MSCS before a sample is taken.

This project has also highlighted the need for an overarching procedure which can be used during each model upgrade exercise to ensure that at any step if there is a turnover of personnel the work can continue in a meaningful and timely manner.

While carrying out the experiments on the new models it was helpful to know the results obtained using the new and old models to understand what the model had done to the results but also understand what the new result would mean to the gasoline blend optimising system as a whole. This stage also indicated the need to have a selection of retained samples to ensure enough testing could be carried out before using the new models on the online system in a real world situation.

The results from the first five online gasoline blends performed using the new EUROBOB_S models have yielded many positive findings, from having the models able to turn an off specification blend into an on specification blend and make positive savings to an already on specification blend. The need to use the optimiser with the models wherever possible to avoid having to perform re-blends on a system that is being run for the better part of seven days a week, and the ability to use the optimiser after a blend has been finished off specification and blend it to an on specification final certification.

13. Recommendations

Using a simple time frame of one year all recommendations can be separated into short term – within one month, medium term – one to six months and long term – six to twelve months.

13.1 Short term: One month

During this investigation many steps have been taken by many people within the blend focus team so creating a systematic procedure of the steps taken by each individual will ensure as the team move onto the next grade of gasoline which the P&E department require updating, the steps required can be carried out more fluidly and by other trained personnel if required, this last part is undesirable but inevitable due to the turnover of staff within the engine laboratory.

13.2 Medium term: One – Six months

Training for more laboratory technicians is required, the engine laboratory technician is currently testing all samples which come through the engine laboratory in batches as time can be scheduled for within the normal testing windows. The technical department which the laboratory resides has put funding in place this year for this modelling task so scheduling time for these jobs is simpler than ever before, but having more personnel trained as well as laboratory shift personnel will mean the samples can be run as and when they are delivered to the laboratory which should alleviate some pressure from the engine laboratory technician who is currently doing the work with the aid of the CSE specialist.

13.3 Long term: Six – Twelve months

Ensure the benefits of the first upgrade is realised moving forward and if improvements are still required repeat the analysis to ensure the site capability can be achieved for EUROBOB_S and when moving onto other grades of gasoline ensure the procedure is followed and used as an active document within the scope of the task. Ensure any updates which are suggested by any people using the procedure are discussed and if required included within the procedure. Attempt to ensure moving forward this job is seen as high significance due to the amount of saving available from each single blend.

13.4 Further work on this system

As stated above the current EUROBOB_S models are now a hybrid of 2014 spectra and 2017 spectra, with the procedure in place to retain all samples going forward, the removal of 2014 spectra from the models becomes a real attainable goal and should not be neglected. Once a suitable number of retained samples has been included within the spectra data, around one hundred and forty to one hundred and sixty samples the requirement for the 2014 spectra will be eliminated entirely.

The FTIR and Grabner analysers in the online system are capable of providing online certification of blends, what this means is at the end of a blend if the analysers have analysed samples within specification throughout the blend no final tank samples would be required as the analysers would be able to certify the tank or cargo of gasoline on specification and release the tank for export or release the cargo for shipping. This would not only reduce the time a ship was required to be on the berth, opening up the berth for another export or import of product but also help to eliminate demurrage charges which currently can diminish savings through optimisation. Online certification would require much tighter limits on final product properties but this is within the capabilities of the analysers. There would also be an increase in the maintenance of the analysers and the validation of each pre blend sample would need to reduce the limits of repeatability. All these factors taken into consideration with the costs required to enable this to take place would make for an interesting project for any future studies.

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15. Appendix

15.1 Preparing Ethanol and Gasoline Blend-stock Hand Blends

Procedure LAB-WKI-030

 Pembroke Plant Revision: 1.0 Status: Issued Issue Date: 21/02/2012	Laboratory Work Instruction	Proc No: LAB/WKI/030
	Title	Originator: B. Manson
	Preparing Ethanol and Gasoline Blendstock Hand blends	Approver: D. Maiden
		Reviewer:
		Review Date: dd/mm/yyyy

Notes: Text shown in *bold italics* indicates a change from previous issues of this document.

This work instruction is uncontrolled when printed. It is the responsibility of the person printing this document to ensure that it is the current version and to either destroy it if isn't or to mark it suitably if kept for reference purposes.

Rev	Date	Description	Author
1.0	21/02/12	New Work Instruction	B. Manson

Safety

Full laboratory PPE, fire retardant lab coat, safety glasses, nitrile gloves and safety footwear, should be worn at all times.

Ethanol is highly flammable and will cause severe eye irritation, moderate skin irritation, respiratory tract irritation and gastrointestinal irritation.

Gasoline blendstock is highly flammable and will cause severe eye irritation, moderate skin irritation, respiratory tract irritation and gastrointestinal irritation.

1. Purpose

This Work Instruction covers and provides instructions on making a volumetric blend of denatured fuel ethanol with gasoline blendstocks.

2. Scope

This Work Instruction covers the use of volumetric glassware for the preparation of volumetric hand blends of ethanol and gasoline blendstocks such as a reformulated gasoline blendstock for oxygenate blending (RBOB), a conventional gasoline blendstock for oxygenate blending (CBOB) or (EUROBOB) etc.

3. References

- 3.1. ASTM D 7717 - Standard Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis

4. Definitions

- 4.1. **Denatured fuel ethanol** - fuel ethanol made unfit for beverage use by the addition of denaturants under formula(s) approved by the applicable regulatory agency to prevent the imposition of beverage alcohol tax.

- 4.2. Denaturants – materials added to ethanol to make it unsuitable for beverage use under a formula approved by a regulatory agency to prevent the imposition of beverage alcohol tax.

5. Procedure

Note: All glassware to be used in the hand blend must be grade A and should be sealed to help prevent the formation of condensation when being chilled.

- 5.1. Chill apparatus, gasoline blendstock samples and denatured fuel ethanol to be used in blending to between 0°C & 4°C.
- 5.2. Determine the ethanol percentage required in the final blend, this information is supplied by scheduling and is stated on the ROP.
- 5.3. Determine how much sample is required to complete all of the required testing and have enough for retention purposes. A minimum of 1.5 litres is required for retention.
- 5.4. Use equation 6.1 below to calculate the amount of ethanol to be blended.
- 5.5. Perform the following steps as efficiently as possible so as to minimise temperature increase and the loss of light ends.
 - 5.5.1. Measure the volume of denatured ethanol required in a suitable volumetric measuring device.
 - 5.5.2. Add the denatured ethanol to the volumetric flask and bring up to the volume with gasoline blend stock.
 - 5.5.3. Thoroughly mix the blend but do not shake vigorously as this will result in light end loss and will affect vapour pressure results.

6. Calculations

6.1. Volume of denatured ethanol for blend

$$V_{de} = [\%E/100] * V_b$$

V_{de} = Volume of denatured ethanol (ml)

$\%E$ = final percentage of denatured ethanol required in final blend

V_b = Target volume of final blend (ml) (e.g. amount of sample required for testing and retention)

15.2 Laboratory Testing of BOB Specification Gasoline

Procedure LAB-PRO-003-A1

 Pembroke Plant	Laboratory Procedure	Proc No: LAB/PRO/003 A1
		Originator: C. Davies
	Title <u>Receipt, Testing and Release of BOB spec gasoline</u>	Approver: D. Maiden
		Reviewer: C. Davies
Revision: 2.4		Last Review: 27/06/13
Status: Issued		
Issue Date: 07/08/14		

Notes: Text shown in *bold italics* indicates a change from previous issues of this document.

This procedure is uncontrolled when printed. It is the responsibility of the person printing this document to ensure that it is the current version and to either destroy it if it isn't or to mark it suitably if kept for reference purposes.

Rev	Date	Description	Author
1.1	03/05/11	5.4.1 Added regarding cleaning the M3 column of ethanol.	C. Davies
1.2	23/8/11	Logo updated post Valero transition	S. Hookey
1.3	21/09/11	5.1.1 Reference to initial off spec tank in a series of blends for a vessel lifting	D.A. Maiden
2.3	27/06/13	Revised throughout	C. Davies
2.4	07/08/14	5.2 & 5.9 revised	C. Davies

1. Purpose

- 1.1. To ensure that BOB specification ethanol hand blends are properly dealt with.

2. Scope

- 2.1. Describe the action to be taken by laboratory staff for ethanol hand blends, All BOB specification gasoline export cargos require the first tank blended to be tested after the addition of ethanol and compared to the relevant specification in addition to base blend testing.

3. References

4. Definitions

- 4.1. BOB – Blendstock for Oxygenate Blending

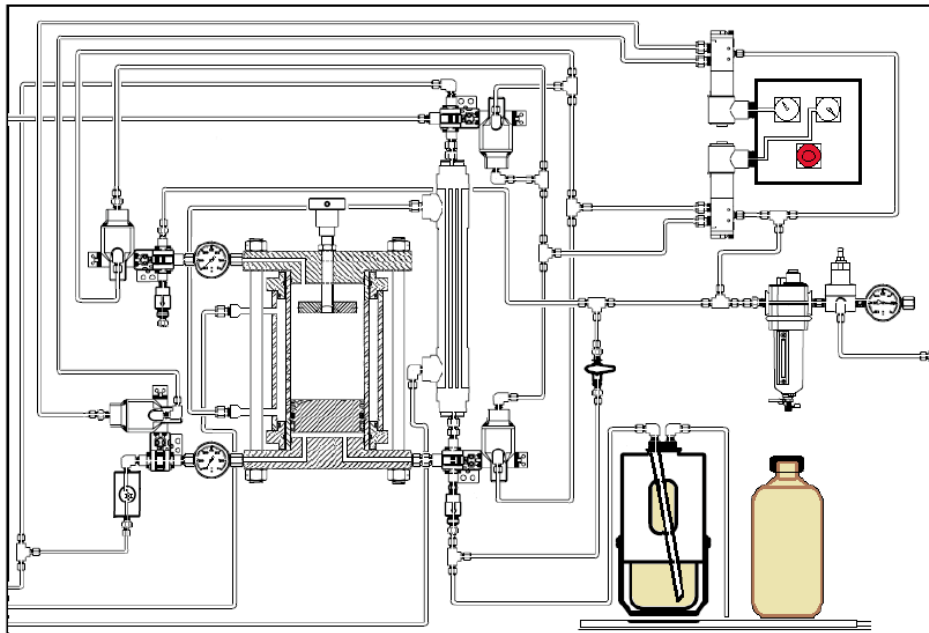
5. Procedure

- 5.1. All tanks that require ethanol hand blends in addition to the base blend will be clearly marked on the ROP by scheduling.

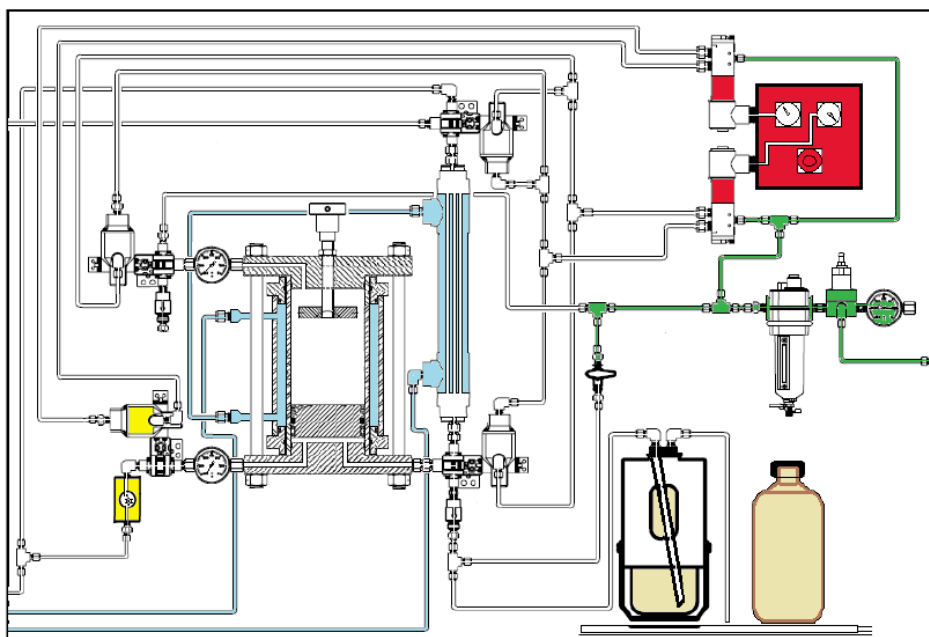
- 5.2. *Testing of the base blend and hand blend should be performed as per the nominated specification and the lab BOB spec gasoline handblend test list.*

- 5.3. On receipt of the tank samples the density should be carried out first to confirm it is uniform, once this is done the ethanol hand blend should be prepared using denatured ethanol (stored in CSR) take care that the ethanol and base blend are at the same temperature prior to making the volumetric blend.
- 5.4. Testing of both the base blend and hand blend should be commenced at the same time with equal priority. Any difficulty in progressing this work due to high workload should be discussed with scheduling.
- 5.5. All calculations required will be done outside of StarLIMS (V/L, driveability, API for Colonial and VLI for European) and can be found via the laboratory intranet page or V:\laboratory\reference\calculations\Mogas
- 5.6. If required the predictive models are available via the scheduling intranet page in the *Gasoline Spreadsheets* folder
- 5.7. Each completed predictive model spreadsheet should be saved in V:\Laboratory\Public\Predictive model spreadsheet. And emailed to GMfg-PEM Scheduling & Quality.
- 5.8. Where testing of the hand blend is carried out the batch should be released based on hand blend results, hard copy specification should always be referred to prior to release.
- 5.9. The CoA for the ethanol hand blend tank should display a **full** set of results for base blend with no specs and all results for the hand blend tests that are included in the *BOB spec gasoline handblend test list with specs, all non handblend batches will only have base blend results and therefore no specification visible on the CoA*
 - 5.9.1. If testing a batch that does not require hand blend testing **do not delete** the ethanol tag in LIMS as it may cause problem if later requested to perform any hand blend testing to check predicted qualities.
 - 5.9.2. Any tests for the handblend that are not requested on the ROP should be left blank in LIMS, do not delete or enter typical type test values.

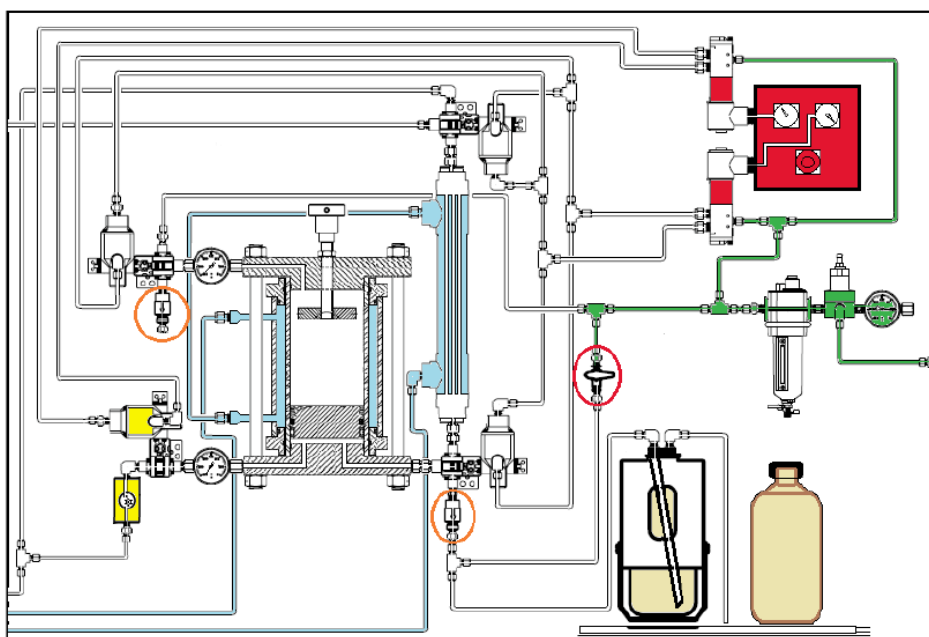
15.3 Manual Sample Collection System MSCS



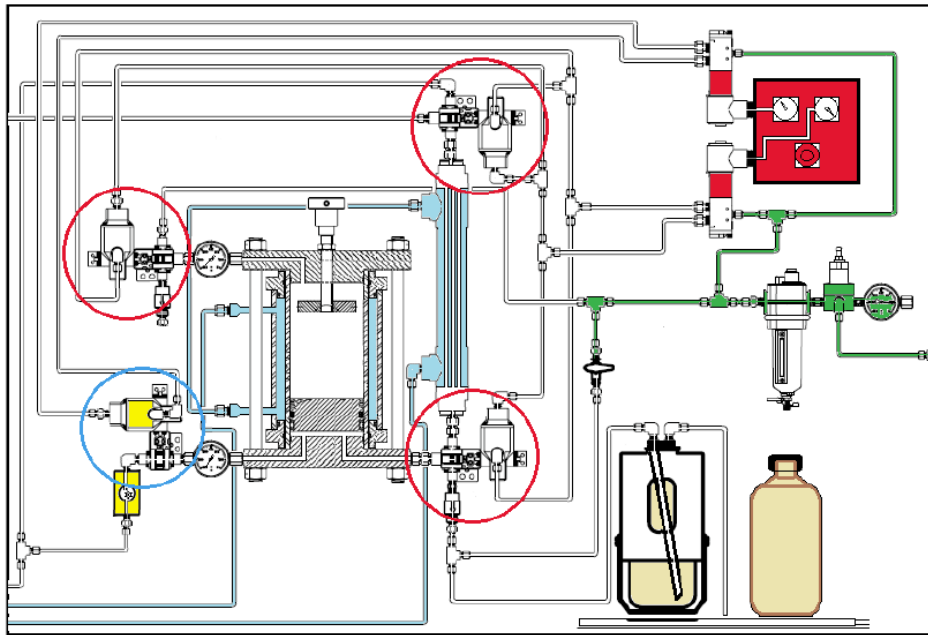
Mission: Simple operation of blend sampler by inserting bottle (brown) and depress button (red) to take a repeatable chilled volume of sample each time.



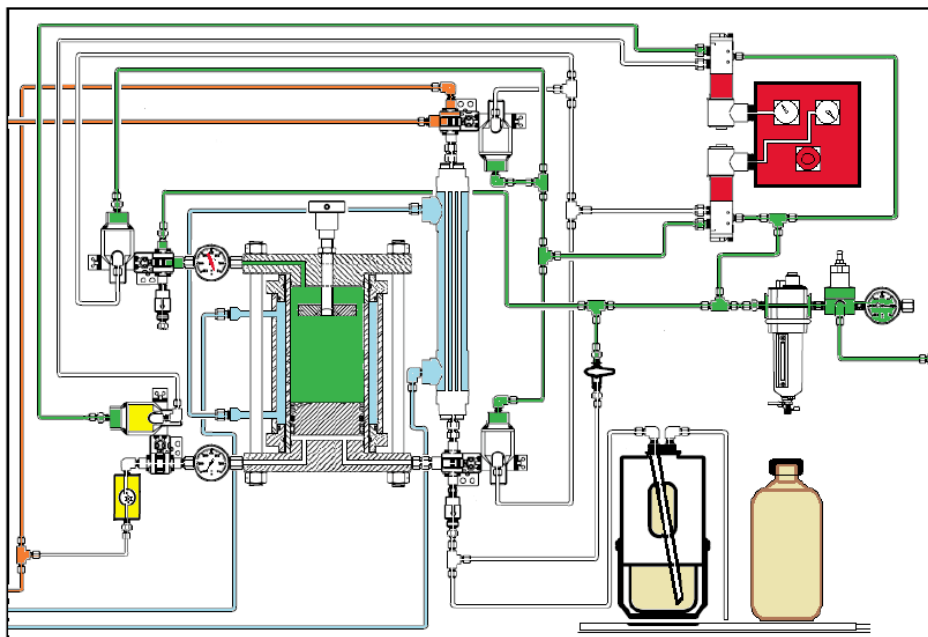
Sampler consists of volume displacement with chiller(blue) controller(red) instrumentation air(green) and purge-sight glass(yellow) container (brown)



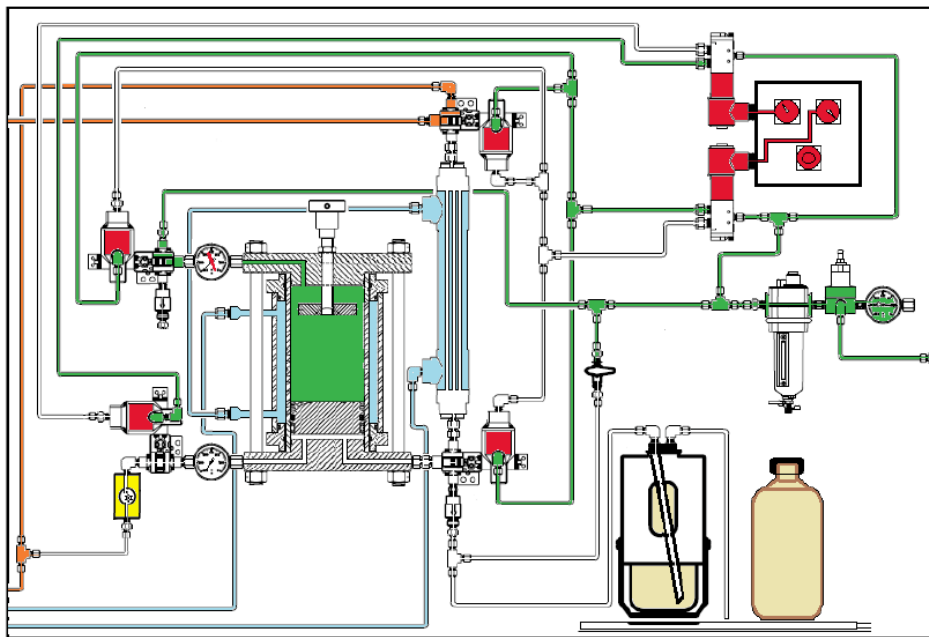
Also contained in the system are two inline relief/check valves (orange circle) that contain 10 PSI springs and a manual purge valve (red circle)



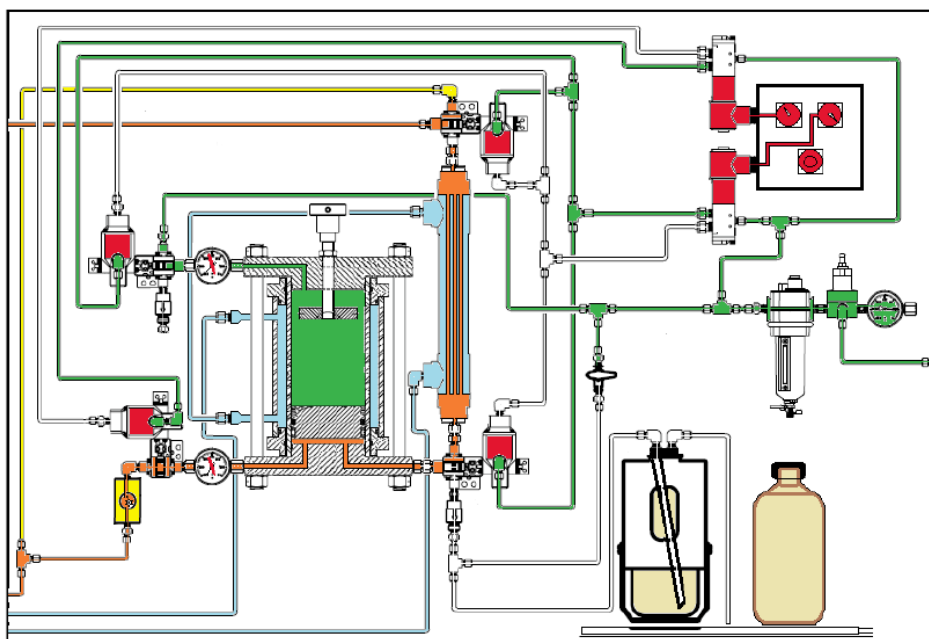
System also contains (3) double acting 3 way valves (red circle) and (1) double acting 2 way valve (blue circle)



Product (orange) would be circulating from inlet to outlet by the first 3way valve (top right of volume chamber) Coolant(blue) thru shell/tube exchanger

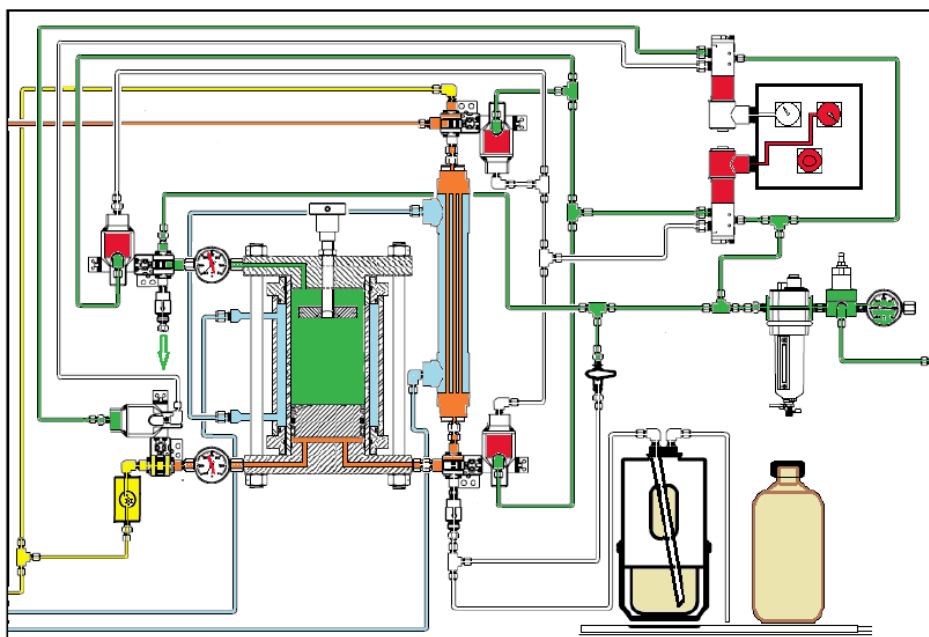


As red button on controller is pushed all double acting valves are rotated by action of air pressure (35 PSI) from 4 way solenoids. Product starts to move



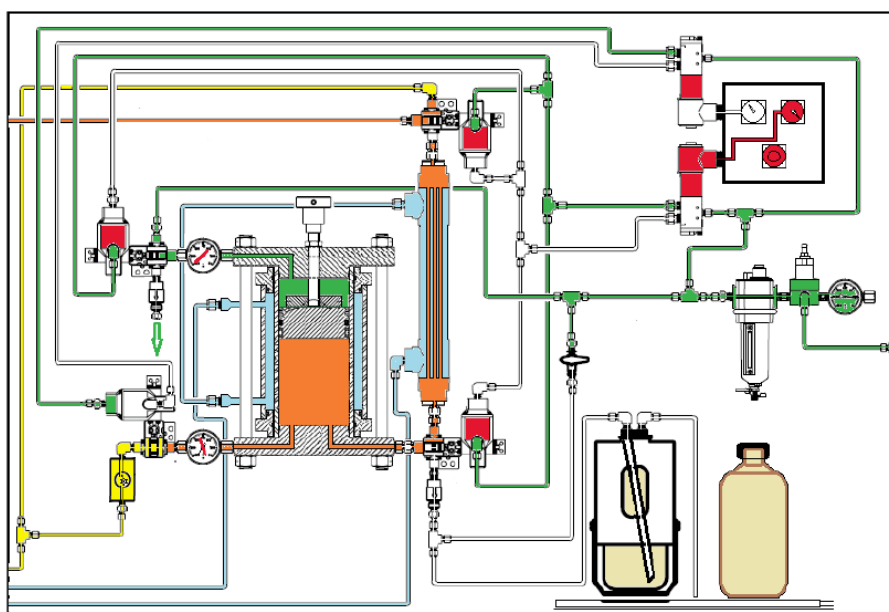
to chiller/volume system since purge valve is opened by solenoid it is being forced through system returning to outlet by differential pressure in loop.

Observing rotating vane in sight glass positive flow can be determined that enough time has passed to allow fresh product to exit to outlet.



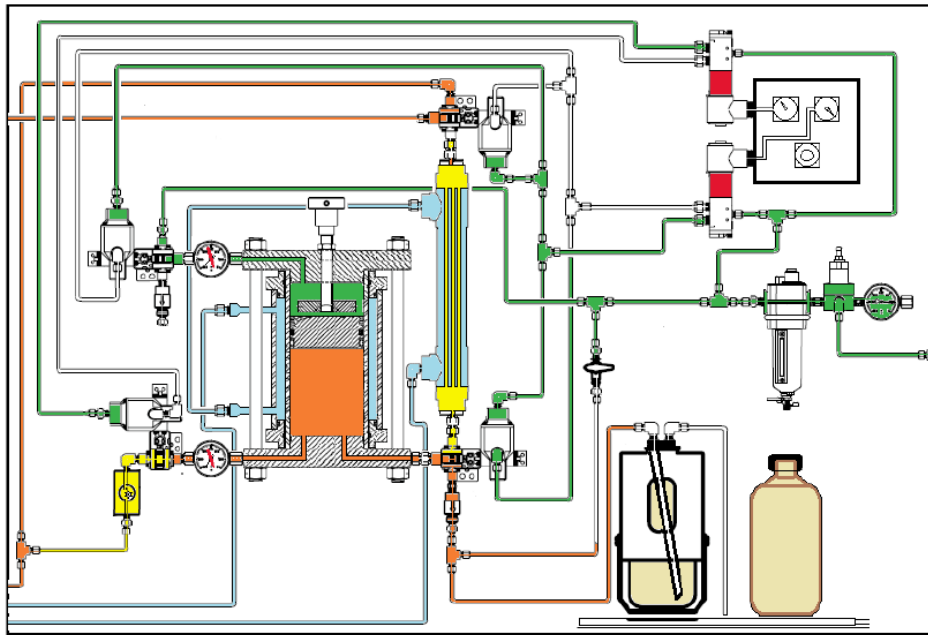
Left resettable timer will be set so purge valve will be deactivated/closed to allow pressure in pipeline to displace piston in volume chamber upward.

As piston moves upward instrumentation air is forced out through inline relief/check with flow restrictor on outlet. Gauge pressure to be observed.



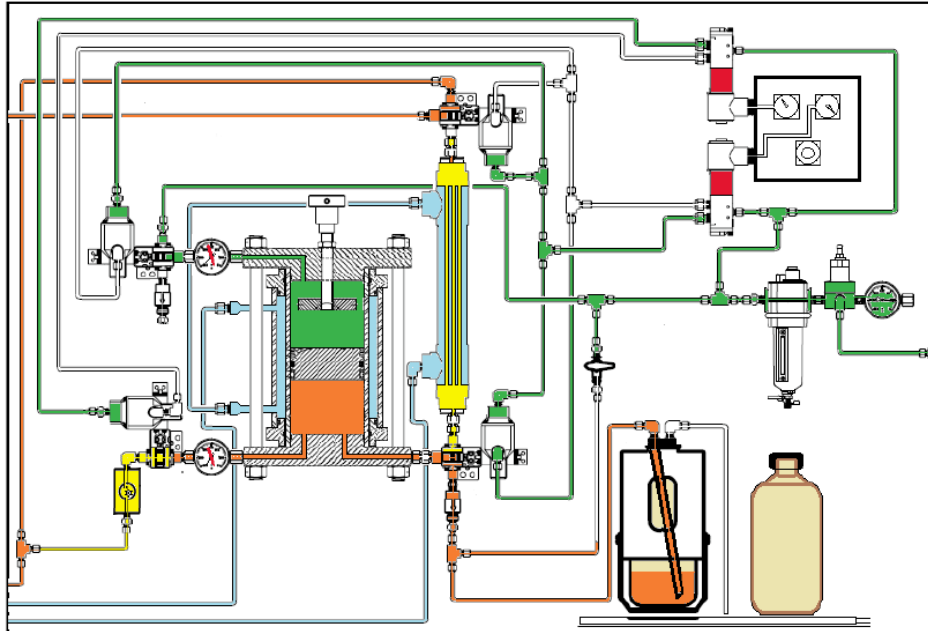
A set amount of time will be set into the right resettable timer to allow product in volume chamber to set to chill down product before deactivation.

When that is determined the right timer will then deactivate and instrumentation air will shift valves to direct product toward sample container



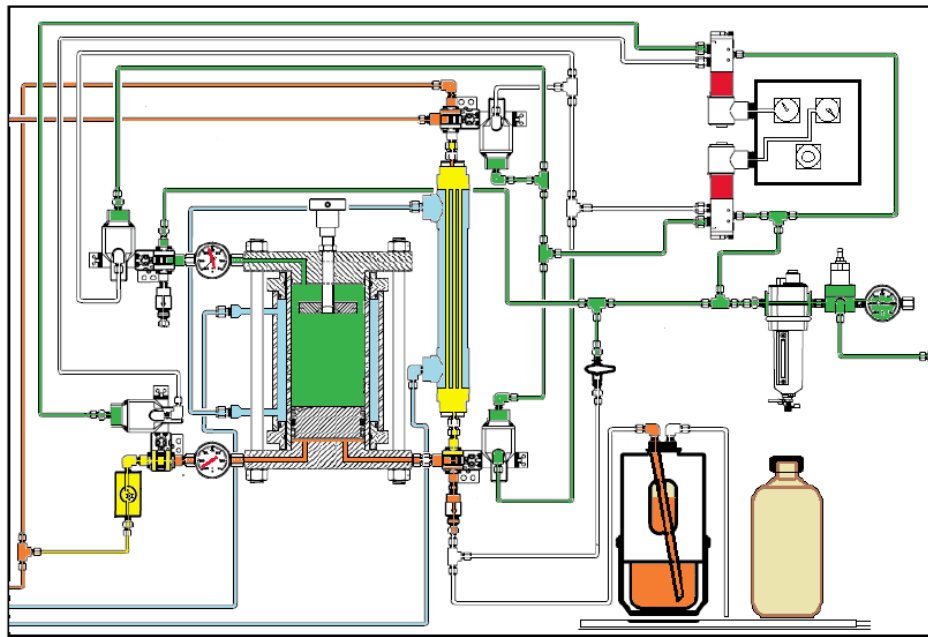
Instrumentation air is then shifted to top of volume chamber forcing piston down and product toward container. Container will be lower due to space

constraint container is shown having tubing sloping upward. As piston moves down product will fill container to desired level. (Knob on top of

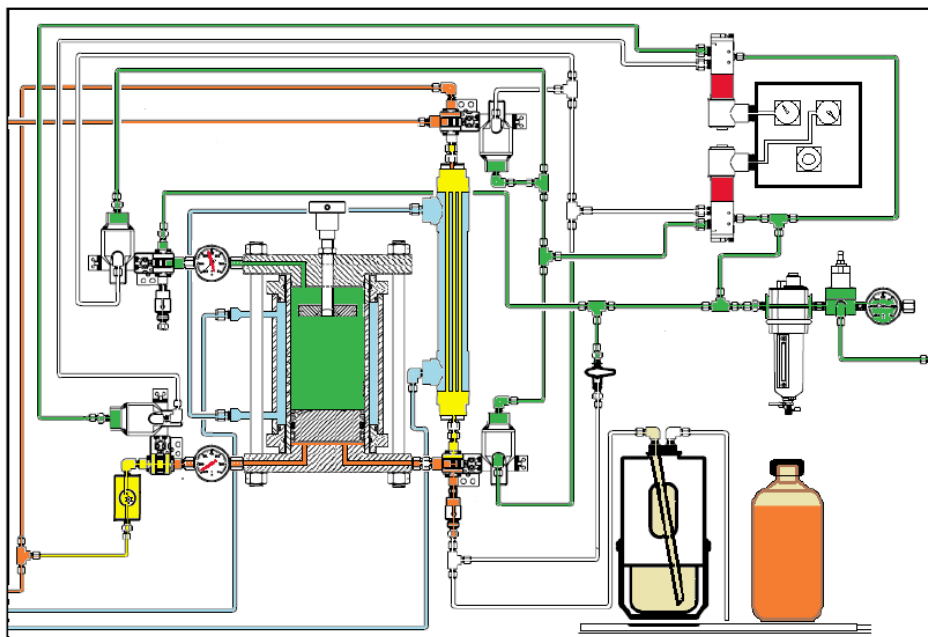


volume container is fine adjustment so exact amount can be displaced into container.) After volume chamber bottoms out inline check will hold volume

back in chamber/chiller area so only the chilled lower portion enters into sample container. The remaining volume will be purged out with next sample



cycle. The amount below the manual purge valve will compress air up into area below valve so when container is removed the air will displaced the rest



of the product into the container allow the finger over the soda straw effect to be broken allowing the remainder of the product to drain into the

container while it is being removed. If so desired the manual valve can be opened purging the rest while there is not container present.

15.4 Management of change Checklist Risk Assessment

Checklist Risk Assessment

EMOC Number & Title	4015602	Assessment Date	03/APR/2018
Assessment Chairperson	PP-HES-JBA-0037 Will Scriven		
Team Members	Will Scriven, Chris Davies, Spencer Harries, Owen Pleasance, Mark Joyce		
Drawing Numbers	N/A		

Checklist for changed items to be addressed in the risk assessment		
<u>PROCESS CONDITIONS</u> Temperature, Pressure, Flow Level Composition Toxicity Flash point Reaction conditions Reaction stability Catalyst Additives, inhibitors, water wash Utilities supply Entrainment Process control Fuel gas composition / quality and instruments Upstream or downstream unit affected Overpressure relief B/D capacity affected Underpressure relief B/D capacity affected	<u>OPERATING METHODS</u> Start up Routine operation Shutdown Preparation for Maintenance Abnormal operation Emergency operation Layout and position of new equipment <u>ENVIRONMENTAL CONDITIONS</u> Liquid, Solid, Gaseous effluent Noise Acceptability of location <u>HEALTH</u> Personal exposure (Ops/Maint). Release consequences Manual handling Noise Legionella-SPI10a/b/11	<u>ENGINEERING METHODS</u> Maintenance procedures RCM assessment, PM Schedule Inspection <u>SAFETY EQUIPMENT</u> Firefighting & Detection systems Means of escape Safety Equipment for personnel <u>ORGANISATION</u> Change to duties New position Position removed Change in building occupancy - numbers Change in building occupancy - time Storage requirements affected <u>Access for:</u> Operation, Maintenance, Vehicles, Plant Firefighting
<u>ENGINEERING HARDWARE & DESIGN</u> Line diagram Wire diagram Plant layout Design pressure Design temperature Materials of construction Insulation:(Addition/Removal/Modification) <i>Shell DEP 30.46.00.31-Gen on Thermal Insulation Section 3 paragraph 3.1</i> <u>Loads on or strength of</u> Foundations Structures Vessels Pipework/Supports/Bellows Surge Protection <u>BUILDINGS</u> Blast hazard boundary**siting of hazard Toxic hazard boundary Building blast resistance Building toxic infiltration rate Water ingress <u>Underground/Overhead</u> Services or Drainage, Equipment	<u>TEMPORARY OR PERMANENT</u> Valves Globe valves in bypass service(high pressure drop) Slip-plates/blinds Restriction devices Filters Static electricity Lightning protection Radioactivity Upstream or downstream equipment affected Rate of corrosion Rate of erosion Vibration Noise Vacuum Isolation for maint. Mechanical-Electrical Fire protection of cables Handrails Ladders Platforms Walkways Tripping hazard	<u>INSTRUMENTATION & CONTROL</u> (include. computer systems) Trips and Alarms Does change affect the control intent of its system? Does change affect any other DCS loops? Does change affect the plant information system? Does change affect any advanced control systems or application? Does change affect any operator Interface? Does change affect any DCS area database functions? E.g. group, trend displays or reports? Has off line software testing been considered? Is standard I/O validation required? Will it foul or affect the operation of mechanical linkages?

Hazard identified	Circumstance	Existing control measures	Unmitigated CxP= <u>Risk</u>	Recommendations (To be transferred to EMOC as Pre-approval, Pre Start-up and Post start up action items)	Mitigated CxP= <u>Risk</u> Level 2 or higher refer to PP-HES-PRO-0011	Name
Composition	Blend off spec during blend	BOSS/analyser informing panel operator blend is infeasible. Inform P&E, make required actions from conversation. ILB taken at regular intervals during blend and tested in the lab. Lab testing of final tank will capture off spec properties.	II X C Business TR	Temporary safeguards for testing - Offline testing carried out prior to upload of updated or new models to online analysers. No ships to be waiting for optimised blend. T3 blend to be selected. Closer monitoring of blend and more frequent ILB samples, if blend suspected to be off spec. Place blend in Ratio. Analysers to carry out checks before blend start.	II X C Business TR	Will Scriven
Composition	Blend off spec after blend completion	BOSS/analyser informing panel operator blend is infeasible. Inform P&E, make required actions from conversation. Lab testing of final tank will capture off spec properties. Reblend tank	II X C Business TR	Temporary safeguards for testing - Offline testing carried out prior to upload of models to online analysers. Minimise impact by having no ships to be waiting for optimised blend. T3 blend to be selected.	II X C Business TR	Will Scriven

Hazard identified	Circumstance	Existing control measures	Unmitigated CxP= <u>Risk</u>	Recommendations (To be transferred to EMOC as Pre-approval, Pre Start-up and Post start up action items)	Mitigated CxP= <u>Risk</u> Level 2 or higher refer to PP-HES-PRO-0011	Name
Does change affect any advanced control systems or application?	BOSS drives blend infeasible	Carry out advice where possible. Put blend in ratio control	II X C Business TR	Offline testing carried out in lab prior to upload of models to online analysers. If problem persists roll back models within analysers to previous version.	II X C Business TR	Will Scriven
Hardware failure	FTIR models uploaded to FTIR analyser	No model updates currently loaded.	I X C Business BA	Offline testing carried out in lab prior to upload of models to online analysers. Ensure backup of old models available during upload. Trained personnel to carry out the upload. Upload to be carried out with blender offline.	I X A Business BA	Will Scriven
Upstream or downstream unit affected	Delayed repair of boss	Site SME and vendor support available. DeltaV blender available	III X B Business TR	Upload of new model to be carried out during working hours with support available. Ensure backup of old models available until testing complete.	III X A Business TR	Will Scriven
Composition	Tank unsuitable for new composition	Composition of gasoline is changing but still gasoline blended to a gasoline tank				

Hazard identified	Circumstance	Existing control measures	Unmitigated CxP= <u>Risk</u>	Recommendations (To be transferred to EMOC as Pre-approval, Pre Start-up and Post start up action items)	Mitigated CxP= <u>Risk</u> Level 2 or higher refer to PP-HES-PRO-0011	Name
Removal of knowledge from blend focus team	Site SME for this task changes position	None	II X D Business TR	Procedure to be written to include steps for offline testing of current model, retain samples for model upgrade, testing of new model, presentation of new model results, upload of model to online system. and precautions for online testing to include (Offline testing carried out prior to upload of updated or new models to online analysers. No ships to be waiting for optimised blend. T3 blend to be selected. Closer monitoring of blend and more frequent ILB samples, if blend suspected to be off spec. Place blend in Ratio. Analysers to carry out checks before blend start.)	II X C Business TR	Chris Davies

74

15.6 2018 FTIR Models

