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Additives and their effect on the properties of winter diesel fuels

Understanding the Cold Filter Plugging Point

Master's thesis in Materials Chemistry

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Gothenburg, Sweden 2018

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A collaboration with Preemraff Lysekil

Cover: a self-service pump for diesel fuel. To the right, a credit card payment terminal. At a Preem petrol station in Avesta, Dalarna, Sweden. Photo by Calle Eklund. November 10, 2010. [CC BY-SA 3.0]. https://commons.wikimedia.org/wiki/File:Dieselpump_Preem_Avesta.jpg

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ABSTRACT

When the temperature of a diesel fuel is reduced far enough, the paraffins, inherent to all diesel fuels, will begin to aggregate, crystallise and form waxy solids. This wax will then block motor filters and thus reduce motor effectiveness and lifetimes. The temperature at which this happens is called the cold filter plugging point (CFPP) and is of constant concern for all fuel producers. Preemraff Lysekil wants to be able to predict the CFPP of a diesel product in order to speed up the analysis process. Experience shows that the CFPP is non-linearly dependant on the properties of the input diesel components and the conventional analysis of the CFPP is slow. This work focuses secondly on the understanding of the CFPP, but mainly on the construction of a CFPP prediction function to be used by Preem in their day-to-day process structure. This task will be performed using the design of experiments (DOE) software MODDE®, which allows for a user to vary several factors at once instead of one factor at a time. Two models are analysed in this work; predicting the CFPP of a diesel blend based on the volume percentages of the input diesel components; predicting the additive dosage needed to reach the desired CFPP based on the cloud point of the input diesel components. There are two datasets used for both models, resulting in four different designs. The two data sets include 24 laboratory samples created by MODDE, and 483 refinery samples created by Preem during the past years. The results show relatively promising results, most of the designs seemingly lacking model validity. The overall most significant and promising design is design B, which predicts CFPP based on the refinery samples with an R2=0,774, Q2=0,757 and RSD=2,848. Future models should be made as to include property variations of the diesel components, for example using the quantitative paraffin distribution of the input component tanks as a basis for the model.

Keywords: CFPP, diesel, prediction model, DOE, wax, MODDE, cold flow properties

ACKNOWLEDGEMENTS

This work is the grand finale of the new chapter of my life that I started when I entered the University and community that is Chalmers. Sometimes I have doubted my decision to start here, and sometimes I felt as sure as could be. Every time my family and friends, both old and new, were there to support me and made me confident that the decision to enter Chalmers was the best decision in my life.

This collaboration with Preem was made together with Stefanus Ivarsson Bergenhem, a close friend and student at the MSc-programme Systems and Control Design whom I want to thank. Stefanus and I worked together continuously to reach the goals of our reports, each using tools and ideas we have learned in our respective MSc-programmes.

Leaving the familiar home of Chalmers to prepare and execute half a year's work at Preem seemed daunting at first. However, the support and sheer enthusiasm showed by our main supervisors Robert Lundin and Peter Holmqvist helped us assimilate to the workplace very quickly. They helped us with every kind of matter ranging from administrative to process-related, while also introducing us to many of their colleagues that would then further assist us in our work.

Mikael Johansson took a lot of time from his regular schedule to help us understand everything about blend optimisation. Malin Govik introduced us to the laboratory and assisted us with all relevant analyses. Thomas Dolff helped us administratively and to come up with new ideas. Jörgen Sauer and his excellent use of Excel helped and allowed us to obtain large amounts of previous diesel samples and lab results very quickly and easily. Dan Andersson gave us a tour of the entire Lysekil refinery, explaining all the different areas and in what way they are interconnected. Göran Fridolf gave us a tour of the control room at Preem, showing us a part of his workday and how our work is connected to the myriad of control software Preem uses.

I sincerely thank you all!

CONTENTS

ABBREVIATIONS

ANOVA	Analysis of variance
C18	Polymer consisting of 18 carbon atoms
CFI	Cold flow improvers
CFPP	Cold filter plugging point (C°)
CP	Cloud point (C°)
DF	Degrees of freedom
DOE	Design of experiments
DSC	Differential scanning calorimetry
EVA	Ethylene/vinyl acetate
F	F-distribution value
GC	Gas chromatography
GO	Gas oil
HGO	Heavy gas oil
MDFI	Middle-distillate flow improver
MS	Mean square
MVA	Multivariate analysis
N	Number of observations
OFAT	One-factor-at-a-time
P	Probability factor
PLS	Partial least squares
POM	Polarising microscopy
PPM	Parts per million
Q2	Model predictive power
r	Repeatability
R	Reproducibility
R2	Coefficient of determination
R2 adj.	R2 but adjusted for the DF of the model
RSD	Relative standard deviation
SD	Standard deviation
SIMDIS	Simulated distillation
SS	Sum of squares
T4	Component tank nr 4
WASA	Wax anti-settling agent

TABLES

FIGURES

INTRODUCTION

BACKGROUND

A selection of the products made at Preemraff Lysekil in Sweden is diesel for use in both Sweden and abroad. When diesel is exposed to cold environments, there is an increased risk of the diesel components waxing. The waxing is a phenomenon which results in motor effect losses as the wax clogs the fuel filters and lines. The temperature at which the waxing indeed becomes a problem is called the cold filter plugging point (CFPP).

There are two main ways to lower the CFPP and thus allow for colder weather before waxing occurs; add certain additives called cold flow improvers (CFI) to the diesel or choose diesel components that have inherently lower the CFPP. The diesel components are distilled crude oil fractions, such as kerosene and diesel oil, which are stored in individual component tanks at the refinery. Mixing the diesel components and the optional additives according to a recipe that follows the required specifications of the buyer is what makes up a diesel product blend.

One of the main difficulties with the CFPP, especially when using additives, is that it is not easy to anticipate the value of the CFPP by looking at the recipe for the diesel. This is because the relationship between a recipe and the following value of the CFPP is non-linear. This issue stretches even further as the cycle time of a conventional CFPP analysis is extensive, meaning that the CFPP is both hard to predict and slow to determine. By finding significant terms, a prediction model would be implemented into diesel optimisation software which would assist the diesel production at Preem, reducing wait times and costs.

Several similar studies have been performed previously, many of which are found in the Fuel (The Science and Technology of Fuel and Energy) journal. Many of the studies touch on the improvement or prediction of cold flow properties of biodiesels. [1, 2, 3, 4, 5, 6] Fewer reports are touching on the cold flow properties of regular diesel. [7, 8, 9, 10] There are very few studies regarding the cold flow properties of regular diesel that is mixed with CFPP additives. [11, 12, 13] Waxing of diesel fuels is relevant today and even more so in the future because of the increased mixing of biofuels, such as the pine tree oil in the Evolution diesel produced by Preem.

GOAL

The goal of this master thesis is to investigate and chart how the additives and diesel components used at Preem will affect the winter properties - mainly the CFPP - of the final diesel product. A rough CFPP prediction function will be created using the design of experiments (DOE) software MODDE®, developed by Umetrics which is part of Sartorius Stedim Biotech. The prediction function construction is also covered in another master thesis on the MSc-programme "Systems and Control Design" at Chalmers University of Technology. The implementation of the prediction function into the optimisation software will not be covered.

BOUNDARIES

This work focuses secondly on the chemistry behind the CFPP which will act as a foundation, primarily on the construction of a CFPP prediction function. Not discussed in this work are the different types of crude oils and in what way they might affect the CFPP and thus the

validity of the prediction model. The model constructed in this work is susceptible to property variations of the component tanks.

THEORY

Definitions of cold flow properties

Three specific temperatures describe the cold flow properties of a diesel solution. The first temperature references the point where the first sign of waxing occurs in the form of small crystals formed around nucleation sites. This temperature is called the cloud point (CP), so named because the wax crystals affect the light passing through the solution, effectively reducing its transparency.

At a specific temperature below the cloud point, the CFPP is reached. The CFPP is defined as the temperature at which the amount of wax that has accumulated on a standardised filter is large enough to block a standardised amount of diesel from passing through the filter within 60 seconds. [14] At even colder temperatures, the crystals are so numerous and so significant in size that the diesel fuel loses its possibility to flow like a liquid. This temperature is called the pour point.

The chemical composition of a standard diesel fuel

Conventional diesel fuel is made up of hydrocarbons, of which 75 % comprises saturated hydrocarbons, primarily paraffin of type n, iso or cyclo. [15] Cycloparaffin is also called naphthene and is saturated alkanes but with ring structures C_nH_{2n} instead. Naphthenes are not to be confused with naphthalenes which are aromatic. The last 25 % of a standard diesel fuel comprises aromatic hydrocarbons, such as naphthalenes and alkylbenzenes. Cyclic structures but the rings have the structure of C_nH_n and are not single bonded. [16, 15]

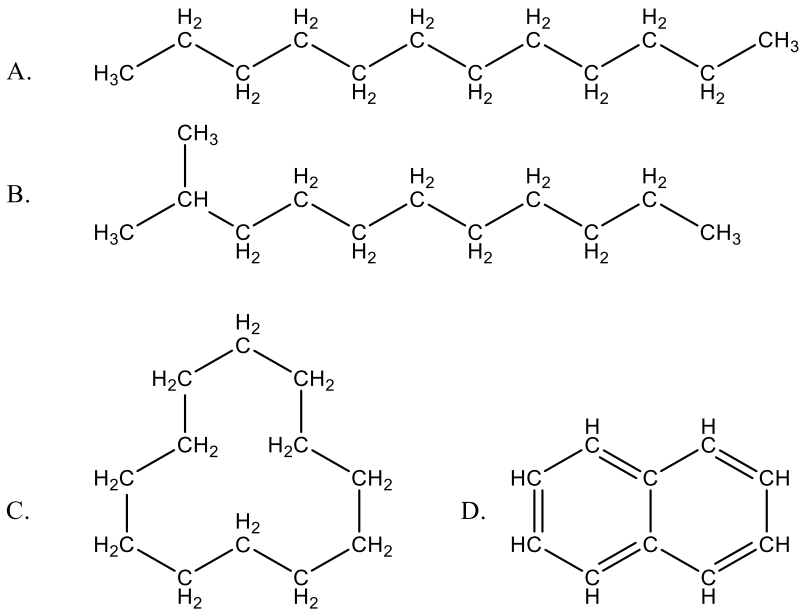


Figure 1. Structures of general examples of the hydrocarbons that make up diesel. A. n-dodecane, normal paraffinic. B. Iso-dodecane, branched paraffinic. C. Cyclododecane, naphthenic. D: Naphthalene, aromatic.

The different types of compounds affect cold flow properties in specific ways, as shown in Table 1. The most interesting parameter for this work is the low-temperature operability,

which is shown to be negatively affected by n-paraffins only. [16] All the other compounds affect cold flow properties positively or not at all.

Table 1. Three parameters and their molecular dependencies. Low-temperature operability is of interest to this work. Essentially as [16].

Fuel property	n-paraffin	Iso-paraffin	Naphthene	Aromatic
Cetane number	+	0/+	0/+	0/-
Low-temp. operability	-	0/+	+	+
Volum. Heating Value	-	-	0	+
+	Indicates a positive or beneficial effect on the fuel property			
0	Indicates a neutral or minor effect			
-	Indicates a negative or detrimental effect			

There are many studies on the low-temperature operability, mainly on biodiesels. Different functional groups seem to influence the CP of a blend. In order they are alkanes, ethers, esters, ketones and diesters, where the latter is the least effective at reducing the CP and the former is the most effective. [1] Degrees of unsaturation of fatty acids affect cold flow properties, where a higher degree of unsaturation yields fuel with superior cold flow performance. [2] A higher degree of desulphuration of the diesel seem to increase the global paraffin content, making the diesel heavier. [8] The CP of a blend depends very non-linearly on the CP of the individual components, where the CP of the heavier fuel dominates. [10] The length of the alcohol chain used for transesterification of a biodiesel affects its CP and CFPP, where a longer alcohol chain results in decreased CP and CFPP. [17]

Waxing mechanisms

Waxing is the crystallisation of paraffin within the diesel blend. When the diesel is cooled, nucleation sites begin to form, where the paraffin start their conglomeration. The crystalline structure that is built up by coagulation of paraffin will form a plate-like structure as the paraffin will mostly only adsorb along the x- and y-axis of the structure. [15]

The crystallisation of wax depends on intermolecular forces, which is generated when the temperature of the diesel blend is reduced below the melting point. There are two steps to the crystallisation; first the nucleation, where liquid molecules aggregate and form crystallites with nucleation sites; then the crystal growth, where the crystal lattices grow and thus give room for more nucleation to occur. [18]

By the dependencies shown in Table 1, it is mainly n-paraffins that tend to cluster together since they are more flexible and will be more affected by intermolecular forces. Iso-paraffins can delay the formation of wax nuclei due to their branching, resulting in unstable waxy solids. The cyclic nature of naphthenes makes them bulky, and they disrupt the wax nucleation or the growth processes, resulting in fewer or smaller crystals. The aromatics are usually good solvents for paraffin waxes. [15]

To view the wax crystal morphology and their crystallisation behaviour, both polarising microscopy (POM) and differential scanning calorimetry (DSC) can be used. When subjected to POM, the wax crystals of the blend will reflect the polarised light and show up as bright white areas on an image. [7] This is an easy way to visualise what the effect of an additive has on a diesel blend.

Fractional distillation

Diesel components are obtained through fractional distillation of crude oil, shown in Figure 2. Within a fractioning column, the input vaporised crude oil is condensed and will split up into different fractions which consist of hydrocarbons with a similar number of carbon atoms. The fractional splitting depends on the boiling points of the various compounds; the heaviest fractions condense early at the hot bottom of the fractioning column, while the lightest fractions condense at the colder top of the column. At the very top of the column, the remaining gas that has yet to be condensed is extracted. [19, 20]

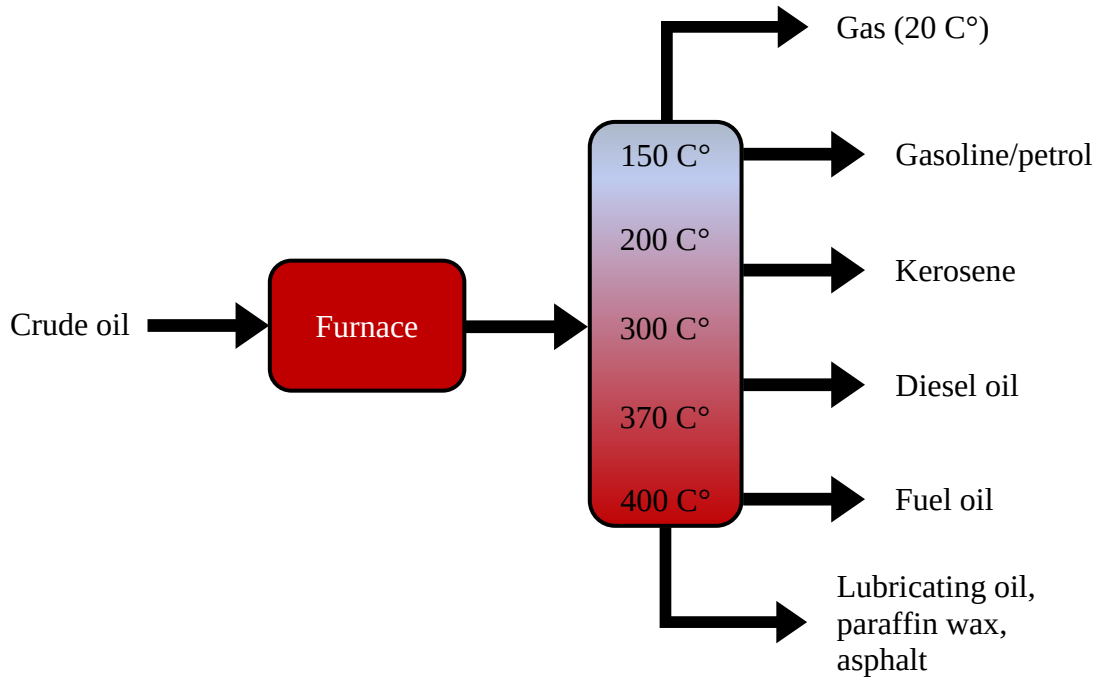


Figure 2. A fractioning column and the products obtained via fractional distillation. Lighter fractions come out the top; heavier fractions come out the bottom. Essentially as [21].

Viscosity and boiling point decreases and flash point increases as one move from the bottom of the column to the top. Regarding the CFPP, this means that the lighter fractions in the upper part of the column yield a low CFPP since they have little tendency to form nucleation sites and crystallise. The more substantial components in the bottom of the column, however, do pose a problem regarding the CFPP, since they have large paraffin that readily forms crystallites. [20]

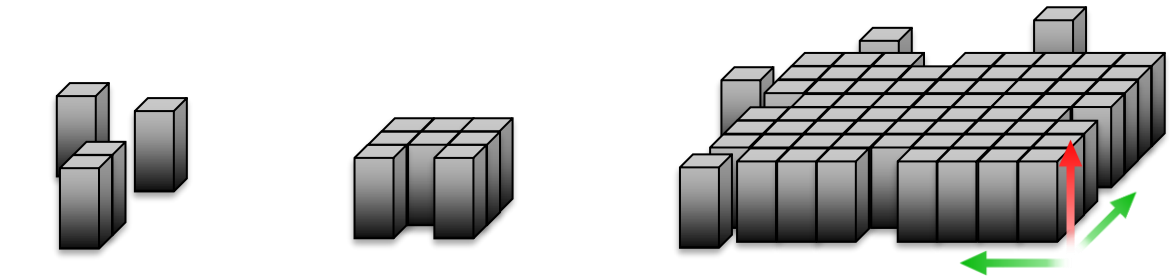
It might then seem desirable to avoid using heavy fractions and only use lighter fractions for a fuel. If all the heavy fractions from the diesel blend were to be removed leaving, for example, C18 and below, the CFPP would still be present but at much colder temperatures. This could be beneficial in that the blend itself would have a low inherent CFPP, even without additives, but the reason why there is heavy paraffin in the blend is due to the increased yield. Removing the heavy paraffin should produce a less energy-rich diesel, which is unwanted.

CFPP additive mechanics

There are two common types of CFPP additives; middle-distillate flow improver (MDFI) and wax anti-settling agents (WASA). MDFI are all polymers which modify the crystal growth towards a particular direction, mainly in needle-like structures. [22] However, even when using MDFI, there will still appear crystals, however they will be smaller and more numerous.

If the amount of crystals make it difficult to avoid blocking of fuel filters, even with MDFI, then WASA can be used in order to help disperse the crystals. [23] Adding WASA to a blend will result in reduced size of wax crystals and increased sedimentation stability. This is done by WASA adsorbing to the wax crystals and, via an electrical polar layer, repelling other wax crystals. [12, 13] Neither MDFI or WASA affect the CP, as they only change the size or morphology of the crystals and do not remove them. [5, 24]

The plate-like crystals that comprise the wax of standard diesel fuel is countered by using CFPP additives such as MDFI or WASA. The additive components are copolymers consisting of a polar polymer backbone with paraffinic side chains. [22] The paraffinic side chains is similar in size to the problematic paraffin in the diesel, allowing for co-crystallisation between the paraffinic side chains of the additive and the paraffin of the diesel. When this happens, the polar backbone of the additive hinders further crystallisation by repelling the non-polar diesel paraffin. Figure 3 visualises the crystalline growth of a diesel blend without a CFPP additive, and Figure 4 shows the effect of mixing an MDFI into a diesel blend.

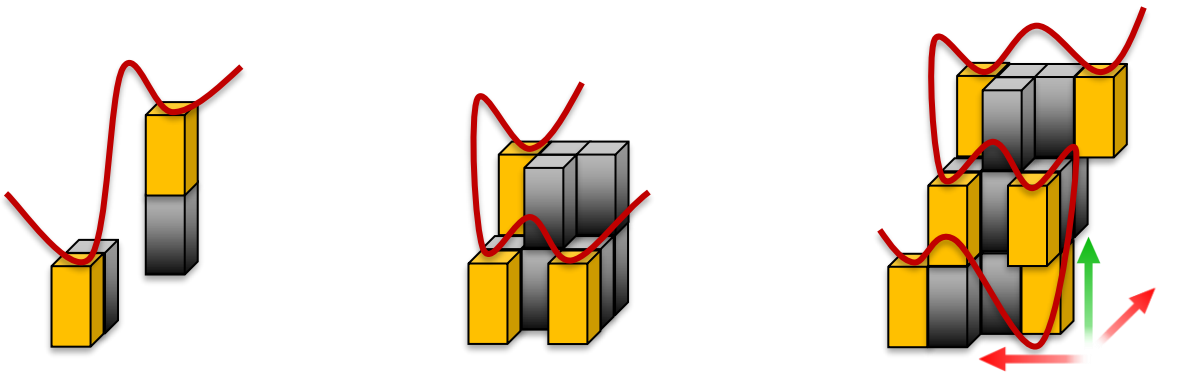


Initial structure just below CP.

Early formation of plate via lateral growth.

Large plate due to unhindered crystallisation along lateral axes.

Figure 3. The crystallisation of wax molecules (black) without MDFI treatment. Large wax plates are formed since the diesel paraffin can crystallise continuously. Essentially as [22].



Initial structure just below CP.

Inhibited lateral growth by the polar backbone of the MDFI

A needle-like structure is formed due to the favoured vertical growth

Figure 4. Co-crystallisation of wax molecules (black) with the paraffinic side chains of the MDFI (yellow) along with the polar backbone (red) of the latter. Smaller wax aggregates are formed as sites necessary for plate formation are blocked by the paraffinic side chains of the MDFI. Essentially as [22].

A previous study that analysed the combination of surfactants and MDFI, namely ethylene/vinyl acetate (EVA), showed that the combination yielded excellent synergistic

effects. This is due to that the surfactants act as nucleation sites for wax growth, and the rapid co-crystallisation between EVA and the wax molecules of the blend. [11]

Prediction model start-up

One of the primary difficulties with creating any prediction model is finding the most relevant properties to include as model variables. General design of such a model would be described as equation (1), showing the general linear model,

$$Y_x = \beta_0 + \sum_{j=1}^{m} \beta_j x_j + \varepsilon_x \quad (1)$$

which is estimated by the following equation (2),

$$E(Y_x) = \beta_0 + \sum_{j=1}^{m} \beta_j x_j \quad (2)$$

In this work, Y_x is the actual CFPP, $E(Y_x)$ is the estimation, or prediction, of the CFPP made by the prediction model, ε_j is an error random variable satisfying $E(\varepsilon_x) = 0$, β_0 is constant coefficient, β_j represents the model coefficients for each process parameter, and x_j represents the values of each process parameter. [25] There are a lot of options of what x_j can represent and determining which x_j to use is an important step in the right direction. This work will mostly focus on using the component tank volume fractions as x_j, as these allow for an early CFPP prediction before the product is mixed.

Another model will also be examined. Instead of predicting the final CFPP of a blend, it might be possible to construct a model that outputs the additive dosage required for a particular difference between CP and CFPP. If one knows the CP of a blend, this model would then say how much additive is needed to reach the desired CFPP.

The methods used for the laboratory analysis of CP and CFPP are shown in Table 2.

Table 2. Standard methods (ASTM) used for the laboratory analyses on the diesel products.

Analysis	Standard method
CFPP	ASTM D6371-17
CP	ASTM D2500-17

Another model that is covered in a similar study includes the use of a DSC to measure the onset and peak temperatures as the sample is cooled and heated. This model can be used to predict the CFPP and CP of a biodiesel blend. [3, 5]

Design of experiments

Before talking about DOE, some terminology must be addressed. Factors include all the input variables and responses are all the output variables. The values of the factors are referred to as levels. [26] This can be explained further by applying these terms to the procedure of baking a cake. In this example, the factors can be sugar, flour, eggs and the oven. These factors are controllable factors, as opposed to uncontrollable factors which are not possible to adjust during experimentation. An example of an uncontrollable factor could be air pressure, which

in most households is not possible to change. Continuing the cake example, the responses could be characteristics such as cake colour, form, taste and consistency. This example is shown in its entirety in Table 3.

Table 3. An explanation of factors (inputs), levels (settings) and responses (outputs), all of which are used in DOE.

Factors (inputs)		Levels (settings)		Responses (outputs)
Flour	→	Grams		
Sugar	→	Grams	→	Taste, colour, consistency, form
Eggs	→	Quantity		
Oven	→	Temperature		

If there is only a few factors and responses to be assessed, the go-to method is usually the one-factor-at-a-time (OFAT) procedure. OFAT means that the value of only one factor will be changed at a time, while the other ones are kept constant. [27] This is repeated for all factors and can yield reliable, albeit slow, results. If there are more than a few factors and responses to be assessed, however, a more robust procedure is required. This is where DOE comes in.

As a branch of applied statistics, DOE involves planning, conducting and analysing experiments to determine which factors will have a significant effect on a given parameter. The way that tests are set up in DOE allows for obtaining the most amount of information possible in the least amount of time and work. DOE accomplishes this by in one way or another changing the values of the factors simultaneously, as opposed to the OFAT method. [27]

DOE usually follows three consecutive steps. First off is screening, a broad range analysis where the most critical factors and their most effective ranges are found. Next up is the optimisation, where an area of optimal performance levels is searched for, while still satisfying all the possible demands of different responses. Lastly, the newly found optimal settings are checked for their robustness. [28]

This work will only perform the screening part of DOE. When the most relevant factors have been found, a model can be created using their coefficients.

METHOD

DATA AND DESIGN SET-UP

In this work, two sets of sample data were used. One data set consists of recipes for and lab results from 483 real diesel product samples (preem blends). The other dataset includes recipes for and lab results from 24 diesel samples (thesis blends), all of which were created in a lab environment for use in this work only.

MODDE was used to prepare all designs. The replicate tolerance of MODDE was changed from the default value of 0,1 to 0,01 as some of the preem blends became replicates when they were not intended to. This change does not affect the thesis blends at all as they do not depend on decimals of that size.

This work contains two different models that might assist Preem. Both models have been determined twice; one for each type of blend (thesis and preem). Thus, there are four designs in total. Designs A and C are based on the thesis blends and designs B and D are based on the preem blends. This layout is further explained in Table 4.

Table 4. Design set-up. An explanation of the combinations of the two blends and two model types included in this work.

	Thesis blends	**Preem blends**
CFPP prediction	Design A	Design B
Additive dosage prediction	Design C	Design D

In order to keep company confidentiality intact, the real names and levels of the component tanks is blocked in this report.

DESIGN A: predicting the CFPP using thesis blend component volume %.

The factors were designed as shown in Table 5. The five formulation factors represent the five diesel component tanks used in the experiment, and they have their respective intervals of total volume percentage derived from their usual ranges at Preem.

The additive concentration and the five component tank fractions were set up as controllable factors. Note that only the five component tanks that make up the formulation factors are considered by MODDE when adding to a total volume of 100 %; the additive is added afterwards, netting a total volume of slightly more than 100 %. However, this should not be a problem as the volume that the additive represents is negligible. [19]

Table 5. Factors used in design A. The levels of all factors and the true names of the component tanks are blocked from view due to company confidentiality.

Name	Abbr.	Units	Type	Use	Settings
XX	Add	ppm	Quantitative	Controlled	XX
XX	T1	% (V/V)	Formulation	Controlled	XX
XX	T2	% (V/V)	Formulation	Controlled	XX
XX	T3	% (V/V)	Formulation	Controlled	XX
XX	T4	% (V/V)	Formulation	Controlled	XX
XX	T5	% (V/V)	Formulation	Controlled	XX

The CFPP is the only response factor included, as shown in Table 6. No minimum, target or maximum value of the CFPP was set.

Table 6. Response used in design A.

Name	Abbr.	Units	Transform	Type	Min	Target	Max
CFPP	CFPP	°C	None	Regular	-	-	-

The objective of this design was screening, as shown in Table 7. This was chosen to find the critical factors that might have a significant beneficial or detrimental effect on the value of the CFPP. D-optimal was the only option, and it allows for a maximum spread of the points in the generated recipes. The standard amount of three centre points was used to observe any variance in blending technique or apparatus usage.

Table 7. Design summary of design A.

Objective	**Screening**	
Process model	Interaction	
Mixture model	Linear	
Design	**D-Optimal**	
Runs in design	19*	
Center points	3	
Replicates	0	
N = actual runs	22*	
Maximum runs	12000	
Constraints	No	
Candidate set		
Extreme vertices	110	
Edge points	0	
Centroids of high dim. surfaces	55	
Total runs	165	
D-Optimal		
Potential terms	Interaction	Quadratic
Number of inclusions	0	
Constraints	No	
Selected design number	25	
Design statistics	G-efficiency	73.5755
	log(Det. of X'X)	12.0408
	Norm. log(Det. of X'X)	-0.11814
	Condition number	1.93055

After MODDE had created a design using the 24 experimental samples according to the input factor levels, they were mixed by hand mixing of the component tanks and additive in a lab environment according to the recipes created by MODDE. The analysis run order of the 24 samples was randomised to avoid any day-to-day aberrations in lab method or technique. The analysis methods yield results similar to the standard methods listed in Table 2 on page 11.

The final step before viewing the results produced in MODDE was to fit the experimental data to a model. In this case, partial least squares (PLS) without pseudo components were used. The model was then sculpted by adding and removing specific model terms. The five formulation factors are required to be a part of the model however it is a free choice whether to include the amount of additive or any interactions between the additive and the different component tanks. The model terms that were included in this design are listed in Table 8. Note that amount of additive was not included as a term in design A, due to lack of confidence. This is explained further in the results and discussion on page 19 and onward.

Table 8. Model terms used in design A.

Full Name	Abbreviation
CFPP	
Constant	Cst
XX	TK1
XX	TK2
XX	TK3
XX	TK4
XX	TK5
XX	TK4*TK4
XX	TK4*TK5

All laboratory analyses performed on the thesis blends were done according to methods yielding results similar to the standard techniques shown in Table 2.

The results and discussion of this design start on page 19.

DESIGN B: predicting the CFPP using preem blend component volume %.

This design was performed with many similarities to design A. However, as the preem blends are not created using MODDE, the preem blend data had to be imported into MODDE and pasted into a custom design. The objective is still screening, and the factors include all the component tanks in design A, but also some additional tanks not used in the thesis blends. The factors are listed in Table 9. Note that the component tanks are listed as quantitative factors instead of formulation factors. This is done as to allow for removal of individual component tanks as model terms later.

Table 9. Factors used in design B. The levels of all factors and the true names of the component tanks are blocked from view due to company confidentiality.

Name	Abbr.	Units	Type	Use	Settings
XX	Add	ppm	Quantitative	Controlled	XX
XX	T1	Fraction	Quantitative	Controlled	XX
XX	T2	Fraction	Quantitative	Controlled	XX
XX	T3	Fraction	Quantitative	Controlled	XX
XX	T4	Fraction	Quantitative	Controlled	XX
XX	T5	Fraction	Quantitative	Controlled	XX
XX	T6	Fraction	Quantitative	Controlled	XX
XX	T7	Fraction	Quantitative	Controlled	XX
XX	T8	Fraction	Quantitative	Controlled	XX

The response is identical to the response used in design A, which is shown in Table 6. As the preem blend data is pasted into MODDE, and not designed within MODDE, the design summary is much more lightweight, as shown in Table 10.

Table 10. Design summary of design B.

Objective	**--**
Process model	Linear
Mixture model	Linear
Design	**Custom**
Runs in design	483
Center points	--
Replicates	--
N = actual runs	483
Maximum runs	12000
Constraints	No

The preem blend data is then fit to a model, using PLS. The model is again adjusted by removing and adding various model terms, with the goal to maximise R2 and Q2, while minimising the RSD. The abbreviated model terms included in design B are listed in Table 11. Note that not all component tanks are included as some were deemed insignificant to CFPP prediction.

Table 11. Model terms used in design B.

Full Name	**Abbreviation**
CFPP	
Constant	Constant
XX	Add
XX	T5
XX	T4
XX	T3
XX	Add*Add
XX	T4*T4
XX	T5*T3

The laboratory analyses previously performed on the preem blends during production were done according to methods yielding results similar to the standard techniques shown in Table 2.

The results and discussion of this design start on page 23.

DESIGN C: predicting additive dosage using thesis blend CP & CFPP difference.

This is a lightweight model; the only factor is additive dosage, as shown in Table 12.

Table 12. Factor used in design C.

Name	**Abbr.**	**Units**	**Type**	**Use**	**Settings**
XX	Add	ppm	Quantitative	Controlled	XX

The response is the difference between CP and CFPP, as listed in Table 13.

Table 13. Response used in design C.

Name	Abbr.	Units	Transform	Type	Min	Target	Max
CP-CFPP	Diff	°C	None	Regular			

As this model does not consider the component tanks used for the blend, the data from the thesis blends is copied and pasted into MODDE, as opposed to design A where it was created in MODDE. The design summary is listed in Table 14.

Table 14. Design summary of design C.

Objective	**--**
Process model	Linear
Mixture model	--
Design	**Custom**
Runs in design	24
Center points	--
Replicates	--
N = actual runs	24
Maximum runs	12000
Constraints	No

The model terms included in design C are listed in Table 15. Note that the only factor in this model is the additive dosage. Thus it is also the only model term apart from the constant.

Table 15. Model terms used in design C.

Full Name	Abbreviation
CP-CFPP	
Constant	Cst
XX	Add

The 24 thesis samples and their analyses were prepared and performed as mentioned in design A. The results and discussion of this design start on page 26.

DESIGN D: predicting additive dosage using preem blend CP & CFPP difference.

This design is very similar to design C with few notable differences. The factor is as the one for design C shown in Table 12, but with a different additive dosage as these are the preem blends and not the thesis blends. The response is identical to Table 13, and the design summary is as the one listed in Table 10 for design B, but with 483 design runs instead of 24. The results and discussion of this design start on page 28.

RESULTS & DISCUSSION

DESIGN A: predicting CFPP using thesis blend component volume %.

Outliers and potential errors

No experiments were excluded from the MODDE worksheet. The residual normal probability plot is shown in Figure 5 and does not show any experiments outside the limits of -4 and +4 standardised standard deviations.

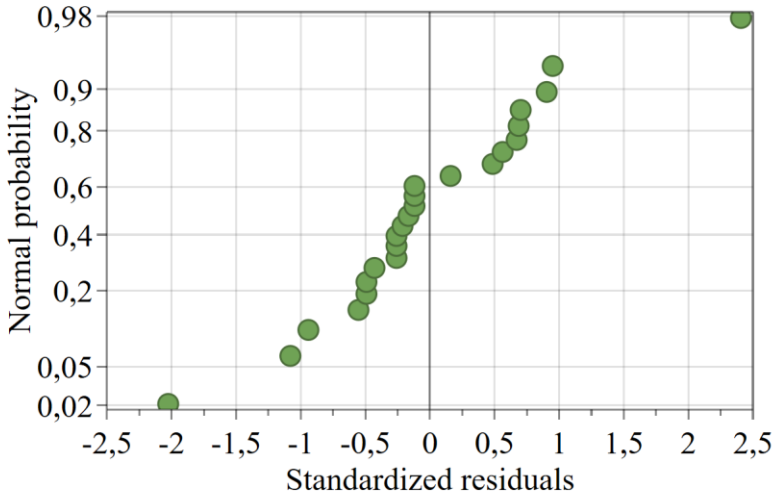


Figure 5. Residuals normal probability plot for design A.

Including dosage of additive as a model term caused issues with MODDE. The contribution of the additive on the CFPP was smaller than all the other interaction terms. This was likely because approximately two-thirds of the 24 samples consist of a significant amount (40 or more volume %) of kerosene, which according to theory does not interact with the CFPP additive. If most of the samples consisted of HGO, the additive coefficient might be more substantial.

Another problem with an additive as a model term is that it made the coefficient plot unable to calculate confidence intervals for all terms. Due to these issues, the additive dosage was excluded as a model term in design A, even though it is expected to have a significant influence on CFPP.

Model robustness

The ANOVA shown in Table 16 shows an RSD of approximately 3,1 °C which is relatively large. The high values of both R2 and Q2 signify a good measure of fit and predictable power in the model. The F-distribution value of 46 for the regression yields a 95 % significance, meaning that the model is statistically good. The F-distribution value of 33 for the lack of fit, however, does also reach the 95 % significance, resulting in a model with significant lack of fit, statistically speaking.

Table 16. ANOVA for design A.

CFPP	DF	SS	MS	F	p	SD
Total	24	21743	905,958			
Constant	1	18872	18872			
Total corrected	23	2870,96	124,824			11,1725
Regression	6	2704,64	450,773	46,0743	**0,000**	21,2314
Residual	17	166,321	9,78359			3,12787
Lack of Fit (model error)	15	165,654	11,0436	33,1309	**0,030**	3,3232
Pure error (repl. error)	2	0,666667	0,333333			0,57735
	N = 24	Q2 =	0,807	Cond. no. =	7,297	
	DF = 17	R2 =	0,942	RSD =	3,128	
	Comp. = 3	R2 adj. =	0,922			

Some of the values in ANOVA are shown as columns in the summary of fit plot shown in Figure 6, along with the model validity and the reproducibility. The model validity is less than 0,25 which implies that there is significant lack of fit in the model; the model error is larger than the pure error.

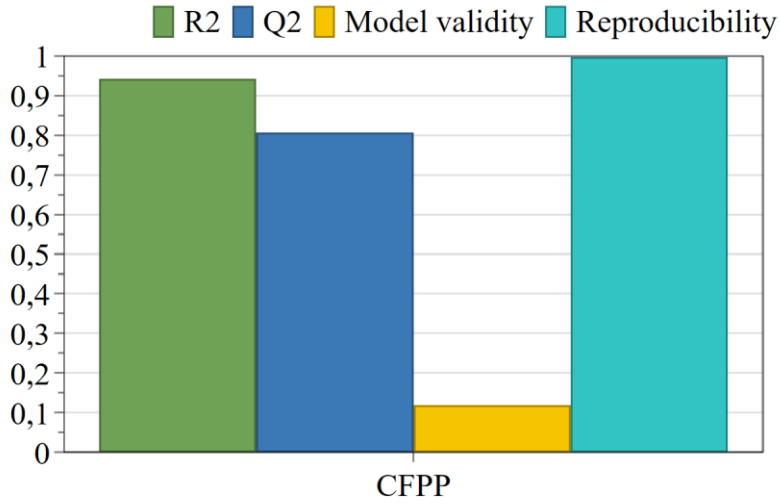


Figure 6. Summary of fit plot for design A.

The predictive power that the relatively large Q2 indicates is shown further in Figure 7 where the observed CFPP is compared to MODDES predicted CFPP. A perfect model would have all the samples perfectly aligned with the black dotted line.

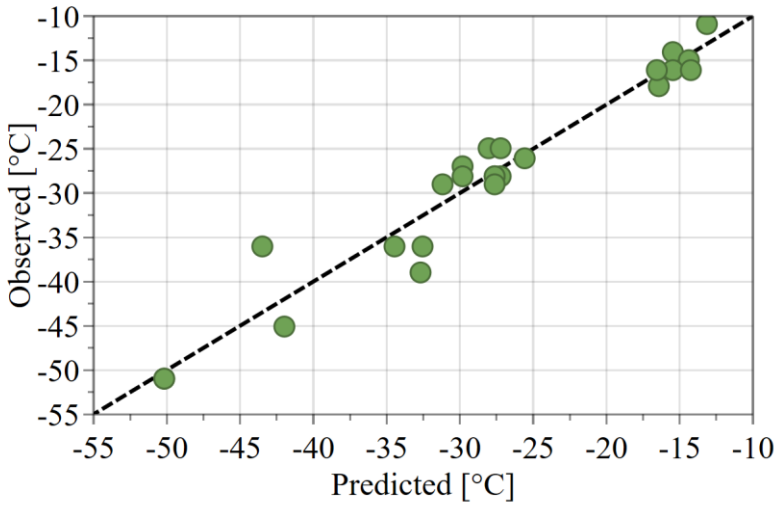


Figure 7. Observed vs predicted CFPP plot for design A.

Significant CFPP contributors

The influence that the factors and the added interaction model terms have on CFPP is visualised in the loading scatter plot shown in Figure 8. The axes represent the X- and Y-weights (w and c) of two PLS dimensions. This shows how the X-variables influence the Y-variables and the correlation structure of the X:s and Y:s. The further a factor is from the plot origin, the more influence it has on the response, which in this case is CFPP. If the factor is in the same quadrant as the response, the influence is in the positive direction, and if the factor is in the opposite quadrant, the influence is in the negative direction.

This means that T4 increases the CFPP by quite a lot, while T3 decreases CFPP by a lesser, but still substantial amount. These are both expected results; T4 contains HGO which should yield a warmer CFPP, and T2 and T3 contains kerosene which has a colder CFPP. Thus, MODDE has shown it is on the right track.

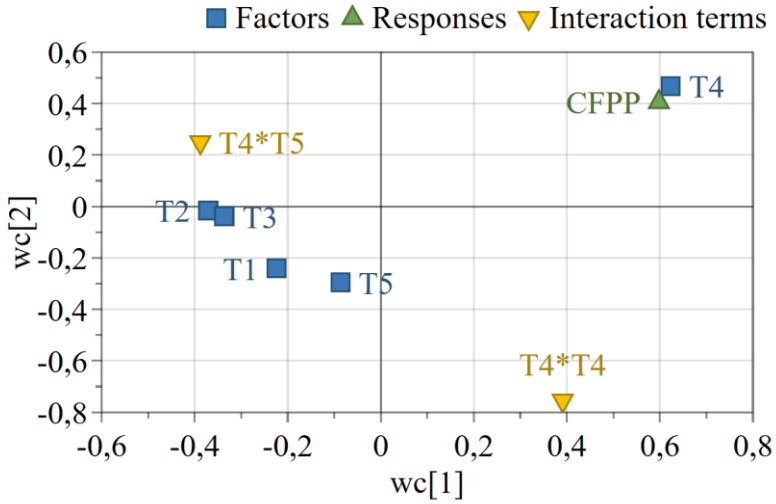


Figure 8. Loading scatter plot for design A.

The coefficient plot in Figure 9 displays the scaled and centred regression coefficients. Again, similar to the loading plots, the most significant contributors to CFPP is shown to be T4 containing HGO and the two kerosene component tanks T2 and T3. The least significant model term shown here is the tank T5 containing diesel oil, having a confidence interval

crossing the y-value of zero. If the factors in this design were not formulation factors but instead quantitative factors, the model terms of the individual tanks could be removed. It would then be an option to remove T5 as a model term. As it stands now, all the five formulation factors must be included in the model.

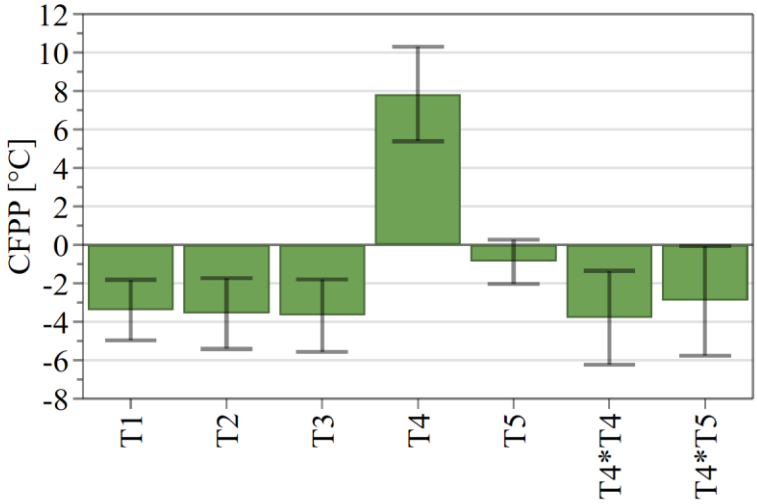


Figure 9. Coefficient plot for design A (scaled and centred).

Prediction function construction

When forming an equation to use as a prediction function, the factors should be multiplied by their respective unscaled coefficients. Table 17 shows the exact values of the unscaled coefficients.

Table 17. Unscaled coefficients for design A.

Model term	Coefficients	Standard error	Probability	Conf. interval(±)
Constant	-27,9739	3,5027	3,7357e-07	7,3901
T1	-25,0387	5,5118	2,8819e-04	11,6290
T2	-21,0790	5,1395	7,4448e-04	10,8434
T3	-20,9317	5,0687	7,0044e-04	10,6942
T4	60,8090	9,0271	3,4855e-06	19,0456
T5	6,2404	3,8410	1,2262e-01	8,1038
T4*T4	-46,0893	14,0586	4,4323e-03	29,6613
T4*T5	-33,4668	15,5213	4,5685e-02	32,7474

Using the unscaled coefficients, a CFPP prediction function can then be constructed as according to the general linear equation (2).

$$CFPP_{PREDICTED} = \beta_0 + x_1\beta_1 + x_2\beta_2 + x_3\beta_3 + x_4\beta_4 + x_5\beta_5 + x_4x_4\beta_6 + x_4x_5\beta_7 \quad (3)$$

Where βi represents the unscaled coefficients, starting with β_0 as the constant coefficient, and x_i represents the factors included in the model.

DESIGN B: predicting CFPP using preem blend component volume %.

Outliers and potential errors

Three preem blend samples were excluded from the MODDE worksheet due to being outside the limits of -4 and +4 standardised standard deviations. Shown in Figure 10 are two residual normal probability plots for design B; the left plot includes all 483 samples, and the right plot has excluded the three deviating samples.

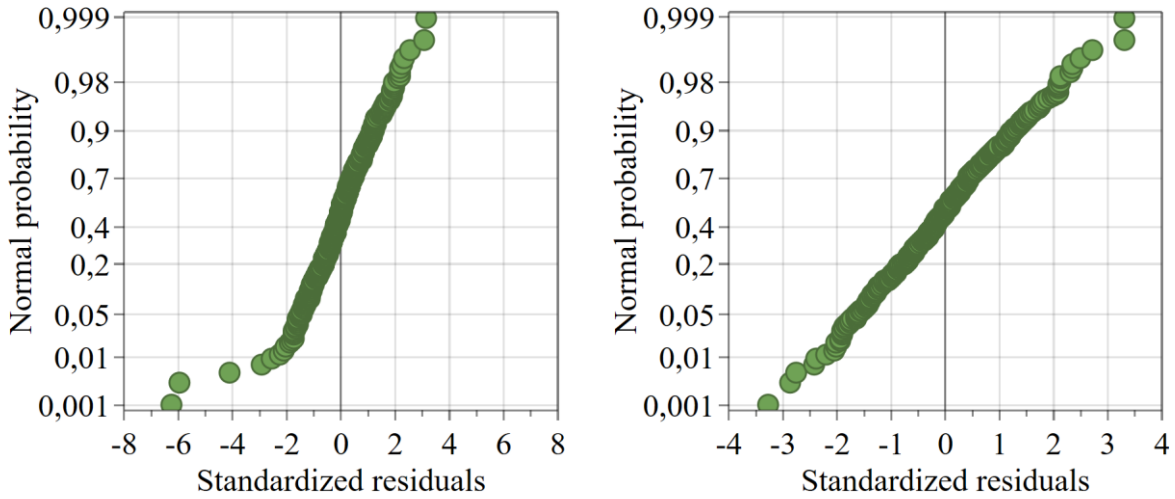


Figure 10. Residuals normal probability plots for design B; the left plot includes all 483 samples; the right plot has excluded three deviating samples.

Model robustness

The ANOVA in Table 18 shows results both good and bad. The pros include a high F-distribution value of the regression, allowing a regression probability significant at 95 % and thus a statistically good model. The values of Q2 and R2 are close but could be higher. The probability of lack of fit is significant at 95 %, meaning the model statistically has lack of fit. The RSD shows approximately 2,8 °C which is relatively large.

Table 18. ANOVA for design B.

CFPP	DF	SS	MS	F	p	SD
Total	480	99507	207,306			
Constant	1	82556,3	82556,3			
Total corrected	479	16950,7	35,3877			5,94876
Regression	7	13121,1	1874,44	231,026	**0,000**	43,2948
Residual	472	3829,6	8,11357			2,84843
Lack of Fit (model error)	436	3772,94	8,65352	5,49753	**0,000**	2,94169
Pure error (repl. error)	36	56,6667	1,57407			1,25462
	N = 480	Q2 =	0,757	Cond. no. =	3,854	
	DF = 472	R2 =	0,774	RSD =	2,848	
	Comp. = 3	R2 adj. =	0,922			

The summary of fit plot shown as Figure 11 agrees with the lack of fit, as the model validity bar is through the floor.

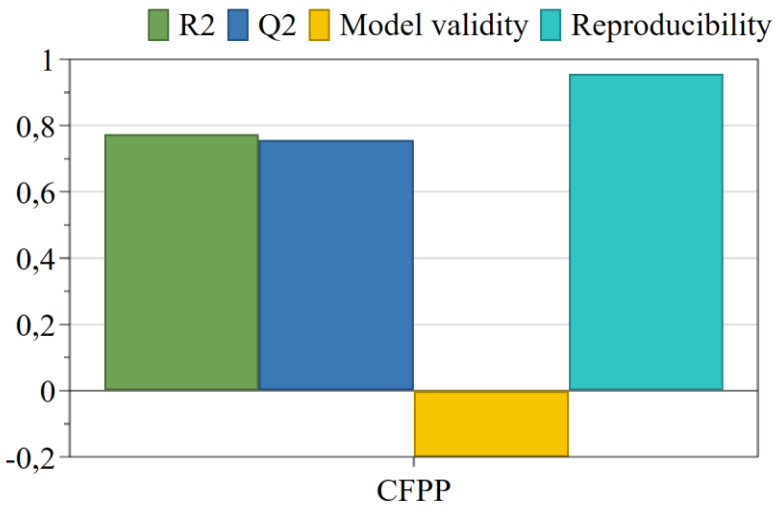


Figure 11. Summary of fit plot for design B.

The data so far does not promise a good prediction model, which is shown further in Figure 12 where the data points are spread far apart around the diagonal of the prediction plot.

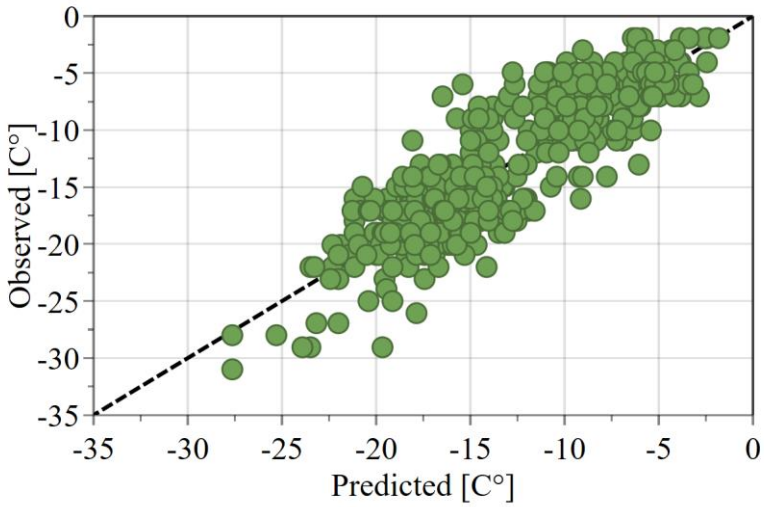


Figure 12. Observed vs predicted CFPP plot for design B.

Significant CFPP contributors

Starting with the loading scatter plot, shown in Figure 13, it can be immediately noted that the additive dosage is the most significant contributor to the CFPP, as it is far from the origin. As the additive factor is in the quadrant opposite to the CFPP response, the contribution is negative which is expected.

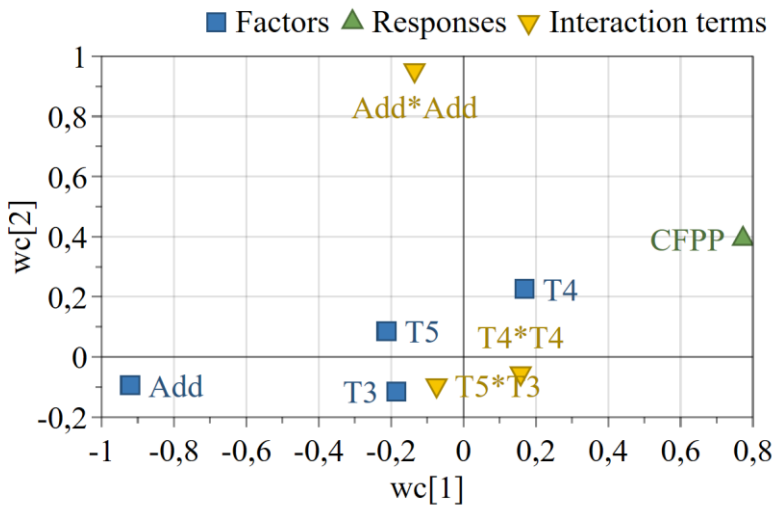


Figure 13. Loading scatter plot for design B.

The coefficient plot, shown as Figure 14, agrees with the loading scatter plot in that the additive dosage massively outweighs all the other model terms regarding CFPP contribution. All coefficients are significant at 95 % probabilities, however, and their confidence intervals are not crossing the y-value of zero.

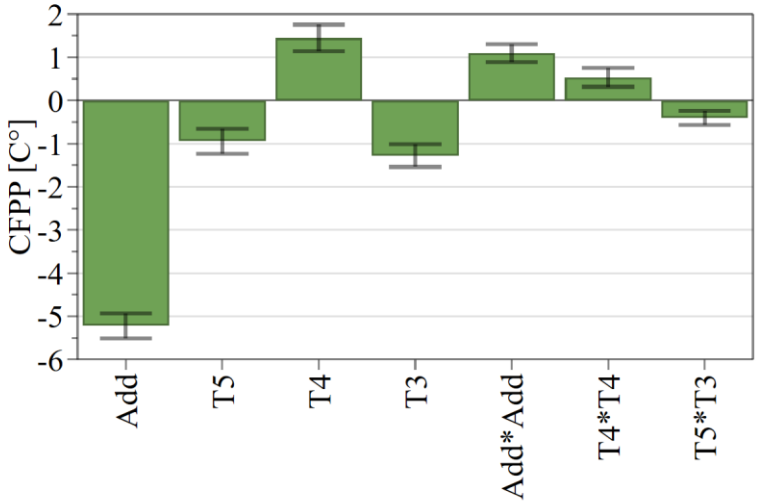


Figure 14. Coefficient plot for design B (scaled and centred).

Prediction function construction

The prediction function would be the same as Equation (3) shown on page 22, except with the new unscaled coefficients of design B, shown in Table 19.

Table 19. Unscaled coefficients for design B.

Model term	Coefficients	Standard error	Probability	Conf. interval(±)
Constant	-3,0871	--	--	--
Add	-0,0419	--	--	--
T5	-0,4296	--	--	--
T4	-7,6586	--	--	--
T3	-8,9517	--	--	--
Add*Add	0,0000	--	--	--
T4*T4	27,5206	--	--	--
T5*T3	-58,8890	--	--	--

Note that the additional unscaled data, such as probability, is missing. This is likely because the value of the unscaled additive dosage coefficient is several magnitudes lower than the values of the other coefficients, resulting in an ill-conditioned matrix. The reason why the additive dosage coefficient is very low is due to the additive factor being input as ppm in the hundreds, while the component tanks are input as fractions between 0 and 1. This is not an issue that affects the model, however, if the additive dosage is input in the model in ppm.

DESIGN C: predicting additive dosage using thesis blend CP & CFPP difference.

Outliers and potential errors

See the same chapter for design A on page 19.

Model robustness

The ANOVA shows very poor R2 and Q2, as well as a high value of RSD. The regression probability is relatively far from being significant at 95 %, which signifies a statistically poor model.

Table 20. ANOVA for design C.

CFPP	DF	SS	MS	F	p	SD
Total	24	6644,41	276,85			
Constant	1	6243,6	6243,6			
Total corrected	23	400,808	17,4264			4,1745
Regression	1	33,0741	33,0741	1,97868	**0,173**	5,75101
Residual	22	367,734	16,7152			4,08842
Lack of Fit (model error)	1	13,2613	13,2613	0,785636	**0,385**	3,6416
Pure error (repl. error)	21	354,473	16,8797			4,10849
	N = 24	Q2 =	0,050	Cond. no. =	1,022	
	DF = 22	R2 =	0,083	RSD =	4,088	
	Comp. = 1	R2 adj. =	0,041			

A seemingly positive side is that the ANOVA shows that the probability of lack of fit is far from being significant at 95 %, meaning the model statistically has no lack of fit. However, this is because the pure error is unusually large.

The pure error is significant because MODDE assumes that all experiments with the same additive dosage are replicates with very different CFPP. These replicates are shown in Figure

15, where each “column” represent a certain level of additive dosage. Replicates exist in all four designs in this work, but they become extreme when one can only choose from three different factor levels. This behaviour is expected in such a model as this.

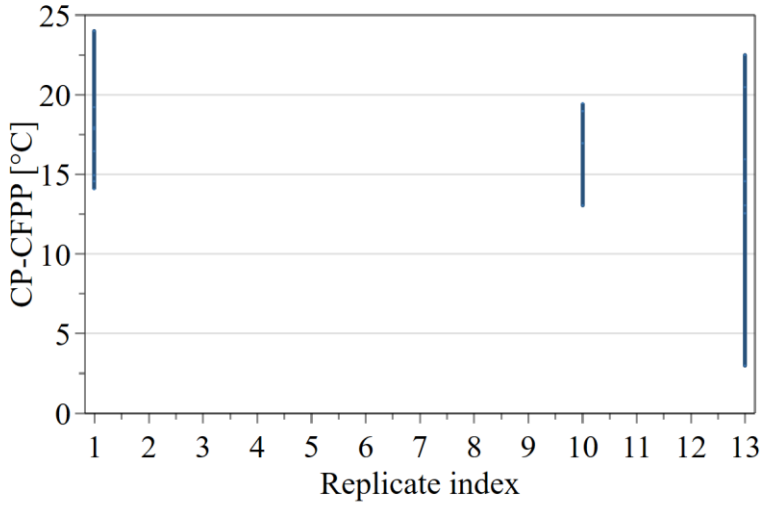


Figure 15. Replicate plot for design C.

The poorness of the model is further visualised in Figure 16 where the only column worth noting is the model validity, which is skewed due to the sizeable pure error.

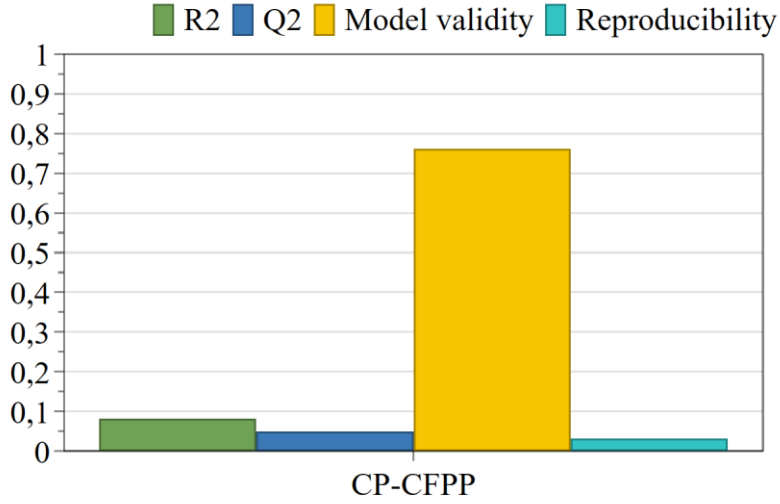


Figure 16. Summary of fit plot for design C.

Not too unexpected, the prediction created by this model will be worthless, as shown in Figure 17 where the data points are severely misaligned with the diagonal.

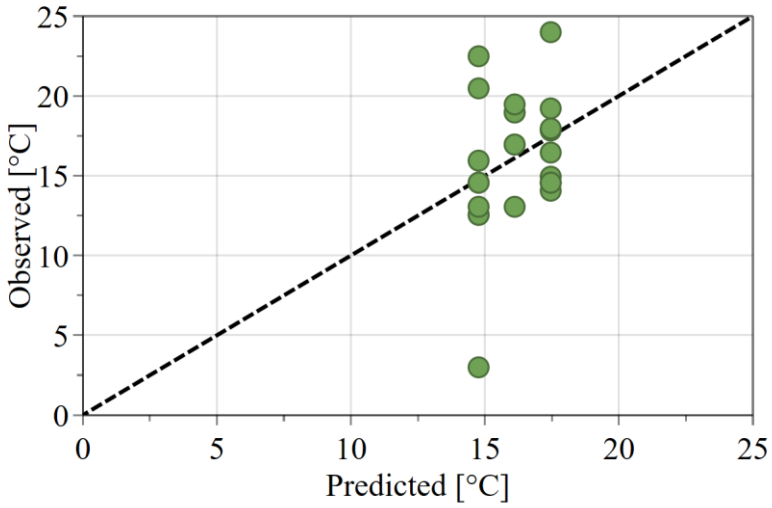


Figure 17. Observed vs predicted CFPP plot for design C.

Significant CFPP contributors

Since there is only one factor included in this model, there are no contributors to compare with. The coefficient plot for the additive dosage is shown in Figure 18. Note that the confidence interval is considerable compared to the column value, further indicating that this is not a significant model.

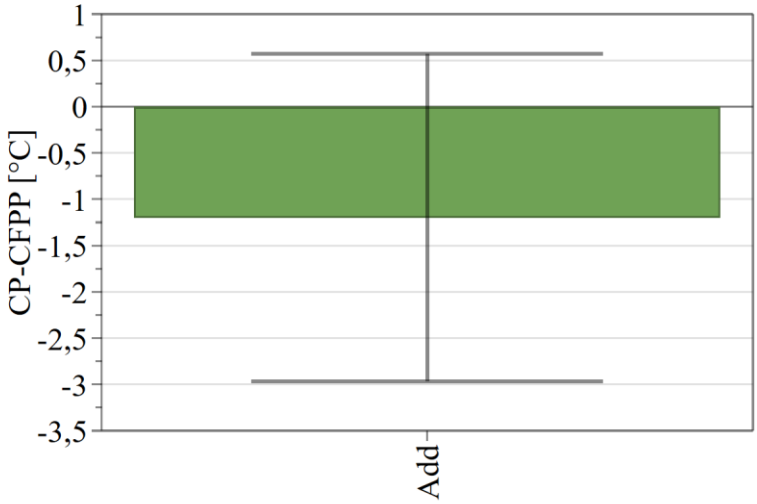


Figure 18. Coefficient plot for design C (scaled and centred).

Prediction function construction

As this model is statistically inferior and of no use, no prediction function will be constructed.

DESIGN D: predicting additive dosage using preem blend CP & CFPP difference.

Outliers and potential errors

See the same chapter for design B on page 23.

Model robustness

The ANOVA shows some promising values. The R2 and Q2 are relatively high and close to each other. The RSD is the lowest of all the designs, sitting at 2,6 °C. The regression

probability is significant at 95 %, and thus the model is statistically good. However, the lack of fit is also significant at 95 %, meaning that there is lack of fit, statistically speaking.

Table 21. ANOVA for design D.

CFPP	DF	SS	MS	F	p	SD
Total	482	52761,5	109,464			
Constant	1	39186,1	39186,1			
Total corrected	481	13575,3	28,2231			5,31255
Regression	2	10346,9	5173,45	767,579	**0,000**	71,9267
Residual	479	3228,44	6,73996			2,59614
Lack of Fit (model error)	19	427,001	22,4737	3,69022	**0,000**	4,74065
Pure error (repl. error)	460	2801,44	6,09008			2,46781
	N = 482	Q2 =	0,759	Cond. no. =	8,02	
	DF = 479	R2 =	0,762	RSD =	2,596	
		R2 adj. =	0,761			

Like design C, the pure error is substantial since the replicates have very different values of CFPP on one given level of additive dosage. The replicates are shown in Figure 19.

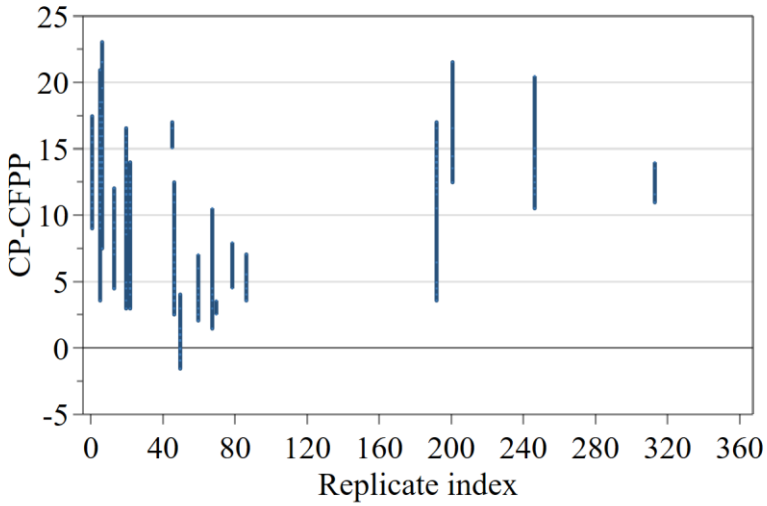


Figure 19. Replicate plot for design D.

The summary of fit plot shown in Figure 20 further shows how close the R2 and Q2 are for design D. However; the poor model validity is also noted, as the model validity column is at the lowest possible value to be shown in MODDE.

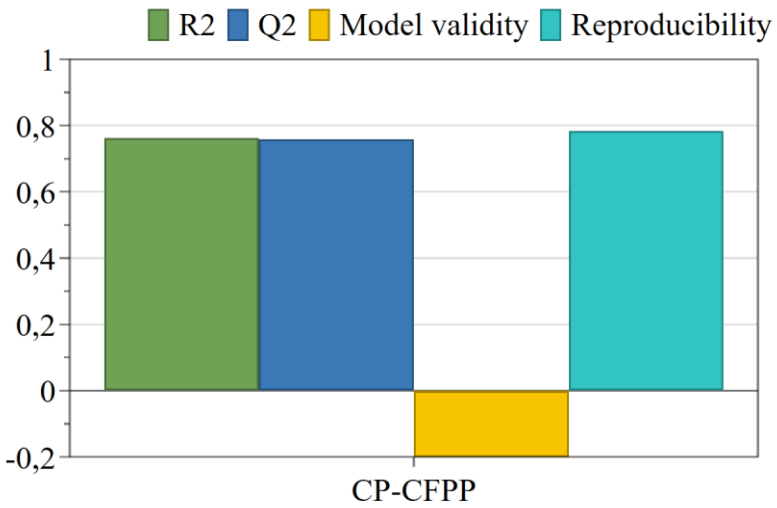


Figure 20. Summary of fit plot for design D.

The observed vs predicted CFPP plot for design D further shows how the predictions made by this model are often far from correct.

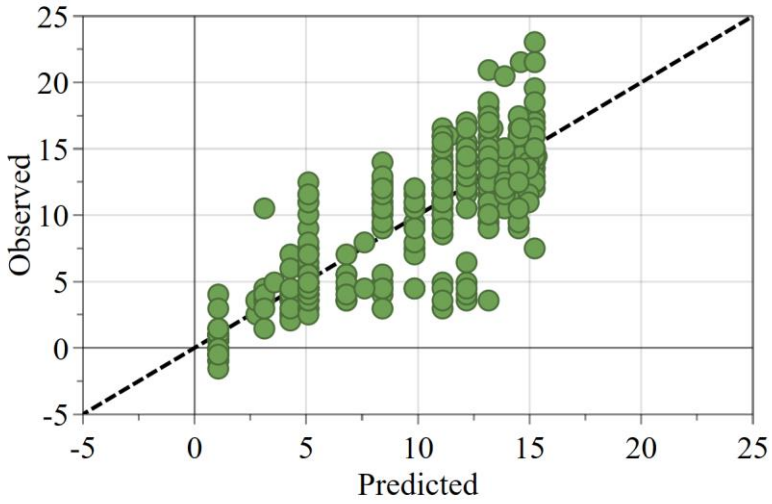


Figure 21. Observed vs predicted CFPP plot for design D.

Significant CFPP contributors

The coefficient plot for the additive dosage is shown in Figure 22. What differs this model from design C is that the additive dosage is also included as a square model term here. Here, the confidence intervals are much more promising than the ones shown in design C; they intervals are small compared to the columns, and they do not cross the y-value of zero.

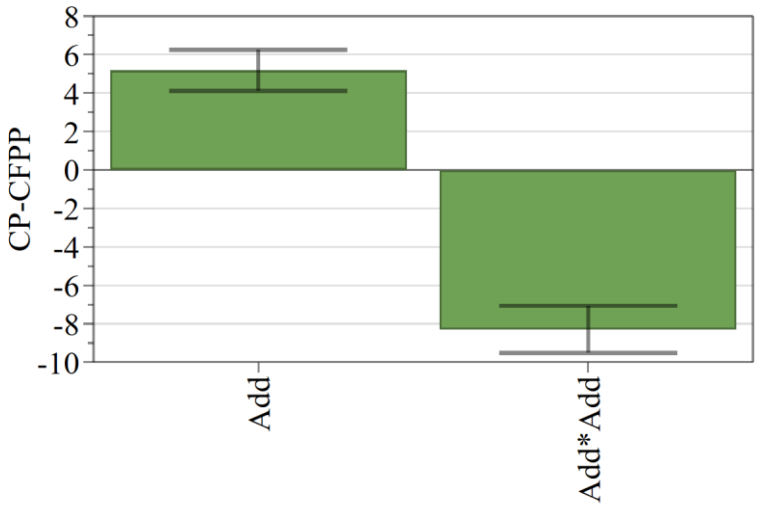


Figure 22. Coefficient plot for design D.

Prediction function construction

The prediction function would be the same as Equation (3) shown on page 22, except with the new unscaled coefficients of design D, shown in Table 22. See the explanation on page 26 as to why the three rightmost columns are lacking values.

Table 22. Unscaled coefficients for design D.

Model term	Coefficients	Standard error	Probability	Conf. interval(±)
Constant	1,03955	--	--	--
Add	0,0435224	--	--	--
Add*Add	-3,31605e-05	--	--	--

CONCLUSION

The goal of this work is to understand and predict the CFPP of a diesel blend. Preem can then apply this knowledge to their production and reduce expensive waiting times and potential delays. There are pros and cons for all four designs that have been performed and analysed in this work. Now, all that is left is to pick out the best version of the respective models.

The first model had the goal to predict the CFPP of a blend based on the volume percentages of the input component tanks and the additive dosage in ppm. The relevant designs here are designs A, using the thesis blends as a data set, and B, using the preem blends as a data set. Here, design B showed the most promise. Both A and B yielded relatively similar results, but when it comes to the data sets, the size does matter. Design B relies on 483 data points, all of which are taken straight from the production at Preem during the past years. This means that design B must be the most prepared for real-world application out of the two. Design B also includes the additive dosage as a model term, something which design A did not find significant. Out of experience, the additive dosage is indeed significant and thus design B again shows the most promise.

The second model had the goal to predict the additive dosage required to reach the desired CFPP based on the CP of the input component tanks. The relevant designs here are designs C, using the thesis blends as a data set, and D, using the preem blends as a data set. Both designs had their faults, but design D showed the most promise. For design C, there were just no advantageous values to be found.

Design B and design D are similar in many ways even though they are different models. This is obviously much because they rely on the same data set. The model validity is low for both designs, something which can be explained by the fact that the properties of the component tanks are not static. Overall, out of all four designs, design B showed the most promise with an R2=0,774, Q2=0,757 and RSD=2,848.

To avoid the problem with varying component tank properties, another model could be constructed that takes the variation into account. For example, a model that predicts the CFPP of a diesel blend based on the quantitative paraffin distribution of the input component tanks. Assuming frequent analysis of the quantitative paraffin distribution of the component tanks, one could just add together all of the input paraffin in order of size. Any property variations of the component tanks would then be noticed as the quantitative paraffin distribution should change. This model would also require the additive dosage as a model term, as the additive should not be noticeable on the paraffin analysis.

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