Fuel 98 (2012) 55–60

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Correlations for Pour Point and Cloud Point of middle and heavy distillates using density and distillation temperatures

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ARTICLE INFO

*Article history:*
Received 10 October 2010
Received in revised form 8 February 2012
Accepted 14 February 2012
Available online 24 March 2012

*Keywords:*
Pour Point
Cloud Point
ANN

ABSTRACT

Linear and Artificial Neural Network (ANN) based correlations have been developed to determine the Pour Point and Cloud Point of middle and heavy distillates. Proposed correlations are based on the most commonly measured properties in petroleum industry i.e. density and distillation temperatures. The linear correlations are presented as such. For neural networks, weights of the optimized network are presented such that the correlation can be easily implemented by the reader.



## 1. Introduction

Stricter fuel norms and quality control have led to an increasing demand for faster and online evaluation of certain refinery stream properties. Accurate estimation of various product properties during the basic engineering phase or simulation can improve the overall economics of refinery. Two such properties are Pour Point and Cloud Point. These properties become important from the diesel cut right down to the high boiling asphalt and tar. Good estimation of these properties is thus of prime importance. These properties are also required during the economic optimization and basic engineering work of refinery. Estimation of these properties for individual streams along-with the simulation studies can be very helpful.

Pour Point [1] of a petroleum specimen is an index of the lowest temperature of its utility for certain applications; it is a measure of the relative amount of wax in oil [2]. In the same way Cloud Point [3] is also an index for the utility of a petroleum product for certain applications measured as the temperature at which a cloud is first observed at the bottom of the test jar. At low temperatures crystals of paraffins form in fuel imposing restrictions on its use. A few degrees below the temperature at which the crystals first appear, the Cloud Point; a crystal network develops in the fluid preventing it from flowing and leading to its Pour Point [4]. So in a way cloud and Pour Points are related and are measures of the paraffin content of the fuel. These properties are also relevant in the context of cold countries where filter plugging in the engine is a problem during cold weather.

The measurement of properties of petroleum and its different streams are based on well-established procedures by international organizations. Pour Point measurement, based on ASTM D97 has no automated method for measurement. The method is tedious and based on observation. The least count of Pour Point using this method is 3 °C [1]. Similar is the case for Cloud Point which is based on ASTM D2500 test method. It is also a test based on observation rather than any automated measurement. It requires the experimenter to record the temperature at which the crystals first appear. In certain cases the appearance of cloud is not very distinct [3].

## 2. Previous efforts

The need for quick measurement of Pour and Cloud Points has led to the development of lot of correlations. Riazi and Daubert [5] developed an empirical correlation using regression for Pour Point which was modified by Chakrabarti [6]. The correlation proposed by Riazi and Daubert [5] was based on specific gravity, molecular weight and viscosity with an average absolute error of 3.89 °C while the correlation given by Chakrabarti [6] was based on specific gravity, molecular weight and distillation temperatures (10% and 90%). However the average absolute error reported by Chatterjee and Saraf [2] using different database and correlations proposed by Riazi and Daubert [5] and Chakrabarti [6] was 8.52 °C and 14.88 °C respectively. Ganguly et al. [7] included the initial and final cumulative volume cuts of the product in their Pour Point prediction method based on ANN. Chatterjee and Saraf

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0016-2361/$ - see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.fuel.2012.02.034

[2] reported the inclusion of mid volume fraction apart from the above properties. Two API correlations [8] for Pour Point are also available, which are based on usage depending on whether kinetic viscosity is available or not. Other parameters being mean average boiling point and specific gravity. Average errors for these correlations with and without viscosity are 3.83 °C and 5.5 °C respectively. Other methods include those based on differential Scanning Calorimetry like the work done by Claudy et al. [9], NMR spectroscopy by Caswell et al. [10], mid IR spectroscopy and neural networks – Pasadakis et al. [11], composition of fuel using NMR and distillation temperatures – Cookson et al. [12].

For Cloud Point estimation, even fewer correlations are available. API correlation [8] uses mean average boiling and specific gravity for the estimation of Cloud Point; average error for this correlation is 4.11 °C. Claudy et al. [9] suggested a method based on Scanning Calorimetry. Caswell et al. [10] also gave a method to determine Cloud Point using NMR spectroscopy; another method was based on NMR and distillation temperatures by Cookson et al. [12]. Pasadakis et al. [11] proposed correlation based on ANN which uses IR spectroscopy to determine Cloud Point.

Correlations proposed in the literature are either not accurate enough or they require lot of information for the estimation of Cloud Point and Pour Point of the mixtures. If the correlation is based on the easily determined properties, the deviation in the experimental and correlated value is large. Though correlations based on IR, NMR, Scanning Calorimetry are accurate and robust, these properties are seldom measured for different refinery streams. In actual refinery operations, sulfur and/or nitrogen content, density and distillation data are the most common properties measured for different intermediate streams and end products. These properties represent overall product quality and performance of the unit. Distillation data and density are also the most important properties for defining refinery streams or assays in process simulation tools e.g. Honeywell's UniSim® Design. Simulation tools use these properties to calculate other thermo-physical properties of streams required for process simulation. Properties like NMR and Scanning Calorimetry are seldom measured in refineries and they cannot be utilized directly for process simulation.

## 3. Correlations for Cloud Point and Pour Point

Present work deals with the formulation of correlations for Pour Point and Cloud Point using the readily determined properties i.e. density and distillation data. Using these properties, Cloud and Pour Point can be estimated during the simulation phase itself. Artificial Neural Networks were employed based on their reputation to recognize patterns even in seemingly unrelated data. The importance of linear correlations however was not disparaged. Linear correlations can be used to reduce the computational cost/resources by sacrificing accuracy. A typical example is refinery economics which is based on linear programming (LP) technique. Proposed linear correlations can be very useful in LP studies.

To form correlations for Pour Point (ASTM D97) and Cloud Point (ASTM D2500), the primary inputs selected were Specific Gravity and Distillation temperatures: 10, 50, and 90 volume percent measured using ASTM D86 method.

### 3.1. Linear correlations

Simplex method was employed for the estimation of regression coefficients for linear correlations. Absolute error was selected as the objective function which was minimized for the estimation of these coefficients. The procedure was repeated with different initial guess values to ensure that the minima of error estimated by the algorithm were the global and not the local ones.

### 3.2. Artificial Neural Networks

To improve the accuracy, Artificial Neural Networks (ANNs) were employed in the second stage of the proposed work. Simple neural network models which were based on the above mentioned inputs were developed. For this purpose 'Stuttgart Neural Network Simulator' (SNNS) version 4.2 [13] was used as a simulator. The data set was divided into three sets, wherein 101 points were used for training, 29 for validation and 15 for testing for Pour Point. For Cloud Point, the division was: 80 data points for training, 23 for validation and 12 for testing. All data sets were scaled linearly between 0.05 and 0.95 using the function below:

$$\overline{x_i} = \frac{a(x_i - x_i^{\min})}{(x_i^{\max} - x_i^{\min})} + b \tag{1}$$

where $a$ and $b$ are constants with the values of 0.9 and 0.05 respectively.

To determine the optimal network, training was performed using logistic sigmoidal transfer function, given as

$$f(net_j) = \frac{1}{1 + \exp(-net_j)} \tag{2}$$

where $net_j$ is the output from a $j$th neuron, given as

$$net_j = \sum_0^n x_i w_{ij} \tag{3}$$

where $x_i$ is the input parameter and the value of $x_o$ is always unity which takes bias into account.

During the training of the network, after each iteration error of validation dataset was estimated to avoid overtraining.

## 4. Database

Honeywell's ASSAY2™ and equity crude assay databases of PETRONAS were used for the development of the correlations.

Table 1 shows the range of inputs and outputs used in the present work. From the minimum $T_{10\%}$ and maximum $T_{90\%}$ temperatures it can be observed that all probable streams being blended into diesel have been covered i.e. from heavy naphtha right up to Atmospheric Gas Oil for Pour Point and Heavy Vacuum Gas Oil for Cloud Point.

For few of the data points distillation analysis was available using ASTM D1160 test method in the database. UniSim® Design Suite R390 was used to convert ASTM D1160 values to ASTM D86 using default option of API 1974 in UniSim® Design. Data was checked for consistency, distillation temperatures (ASTM D86), Pour Point (ASTM D97) and Cloud Point (ASTM 2500) all in °C.

For the proposed neural network models, a thorough examination of the input–output data was done to identify and eliminate outliers. Next inputs and outputs were scaled to avoid numerical overflows due to very large or small value of weights. Also properly scaled inputs and outputs enhance the overall network performance [14]. A small margin during scaling was kept to facilitate extrapolation on either side of the range. Also it deals effectively with the problem of large output layer weights which may lead

**Table 1a**
Minimum and maximum values of inputs and outputs for Pour Point correlation.

| Property | Standard | Units | Minimum | Maximum |
|---|---|---|---|---|
| Specific gravity | ASTM D4052 | – | 0.7612 | 0.9892 |
| $T_{10\%}$ | ASTM D86 | °C | 144.00 | 506.67 |
| $T_{50\%}$ | ASTM D86 | °C | 149.00 | 514.56 |
| $T_{90\%}$ | ASTM D86 | °C | 161.00 | 525.32 |
| Pour Point | ASTM D97 | °C | −74.00 | 72.00 |