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

Arpit S. Maheshwari [a], Jitendra G. Chellani [b,*]

[a] Chemical Engineering Department, Birla Institute of Technology and Science, Pilani 333 031, India
[b] Honeywell Technology Solutions Laboratory Pvt. Ltd., 151/1, Doraisanipalaya, Bannerghatta Road, Bangalore 560 076, India

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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

* Corresponding author. Tel.: +91 80 26588360; fax: +91 80 26584750.
E-mail address: chellanijg@gmail.com (J.G. Chellani).

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[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 jth 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

Table 1b
Minimum and maximum values of inputs and outputs for Cloud Point correlation.

Property	Standard	Units	Minimum	Maximum
Specific gravity	ASTM D4052	–	0.7883	0.9548
$T_{10\%}$	ASTM D86	°C	183.00	478.00
$T_{50\%}$	ASTM D86	°C	188.00	503.00
$T_{90\%}$	ASTM D86	°C	200.00	545.00
Cloud Point	ASTM D97	°C	−54.00	52.00

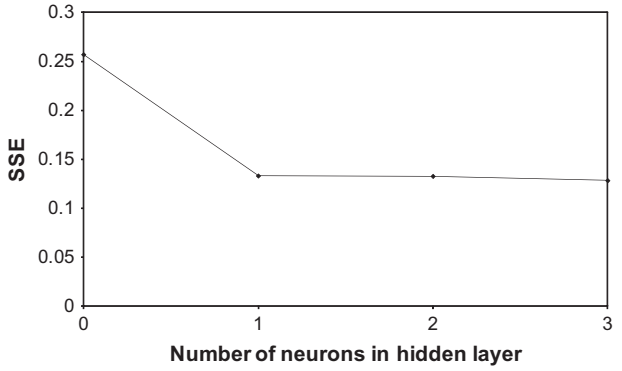

Fig. 1a. SSE vs N for Pour Point correlations.

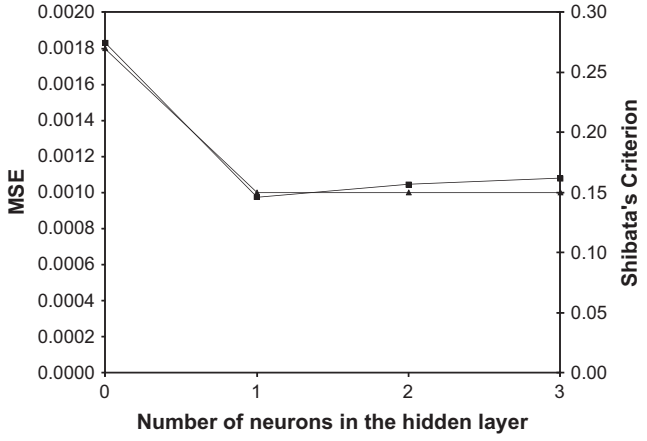

Fig. 1b. MSE and SC vs N for Pour Point correlations, MSE (▲), Shibata's Criterion (■).

to numerical overflows that might arise when generating the outputs of 0 and 1 using the logistic sigmoid function.

5. Results and discussions

The primary inputs, distillation temperatures and specific gravity were chosen because of the ease of determination of these properties and their availability in the refinery simulation studies. All important refinery streams are at least characterized by these properties as was observed in the data and actual refinery operation.

Number of neurons in the hidden layer was varied to select an optimum network. Since increasing the network complexity which means essentially increasing the number of weights usually leads to a reduction in SSE, there is a tradeoff between accuracy and complexity. Shibata's Criterion is a good compromise between the two and has thus been chosen as a selection criterion for the network over SSE.

Table 2a
Weights for Pour Point network.

Layer	Source neuron	Target neuron 5
Input	1	−1.00789
	2	0.31140
	3	1.90381
	4	1.00590
	Bias	0.45724
		6
Hidden	5	12.65352
	Bias	−10.11953

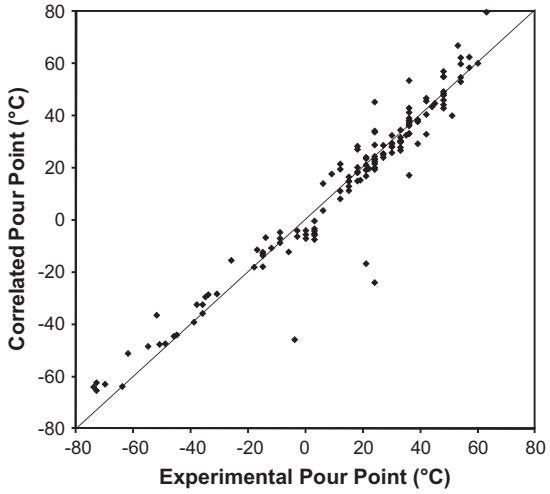

Fig. 2a. Parity plot for Pour Point using linear correlations, i.e. Eq. (5).

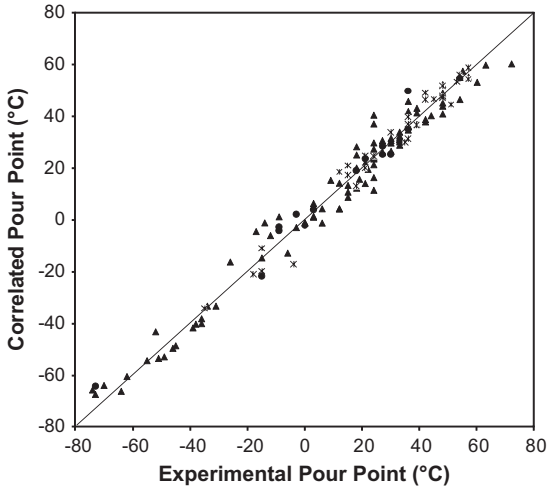

Fig. 2b. Parity plot for Pour Point using ANN with weights corresponding to Table 2, training (▲), validation (∗) and testing datasets (•).

It is defined as:

$$\text{SHIBATA} = \frac{\text{SSE}(n+2p)}{n} \tag{4}$$

SHIBATA is the Shibata's Criterion, SSE is the sum of squared errors, n is the number of observations (sample size), p is the number of parameters, to be estimated (weights or regression coefficients).

Table 2b
Comparison of various correlations for Pour Point.

Correlation	Specific gravity		MeABP (°C)		Pour Point (°C)		Average absolute error (°C)
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	
API	0.8000	1.0000	171.29	560.18	−39.82	54.63	11.15
Linear	0.7612	0.9892	150.01	514.62	−74.00	72.00	5.75
ANN	0.7612	0.9892	150.01	514.62	−74.00	72.00	3.88

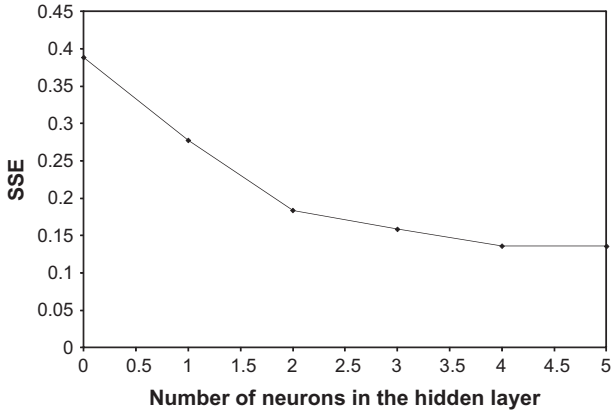

Fig. 3a. SSE vs N for Cloud Point correlations.

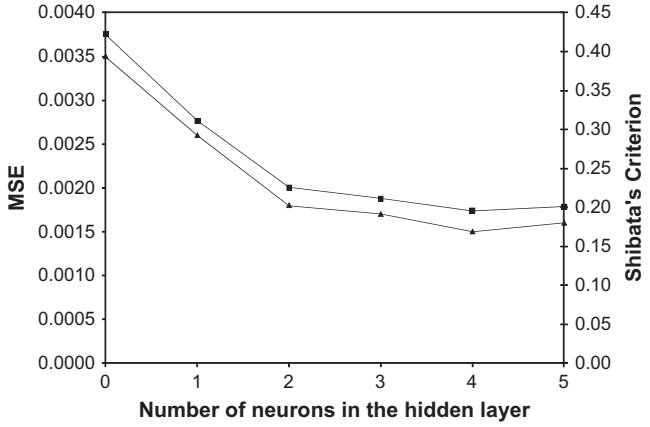

Fig. 3b. MSE and SC vs N for Cloud Point correlations, MSE (▲), Shibata's Criterion (■).

Table 3a
Weights for Cloud Point network.

Layer	Source neuron	Target neuron			
		5	6	7	8
Input	1	−0.78200	1.91866	−3.45854	3.95283
	2	5.80997	−2.24016	−2.57958	0.45573
	3	3.38192	−4.75801	−0.10295	3.67084
	4	−4.05086	−6.59887	−1.06323	8.65604
	Bias	−4.50102	1.11550	2.43885	−6.66242
		9			
Hidden	5	5.83627			
	6	−5.46574			
	7	5.16181			
	8	2.83176			
	Bias	−3.34448			

Different optimization algorithms were tried, among them Scaled Conjugate Gradient (SCG) gave best results. Number of neurons in the hidden layer was varied from 0 to 5 and the networks with one and four neurons in the hidden layer were found to be optimum for Pour Point and Cloud Point respectively. Hence our final networks were 4–1–1 for Pour Point with 7 weights and 4–4–1 for Cloud Point with 25 weights.

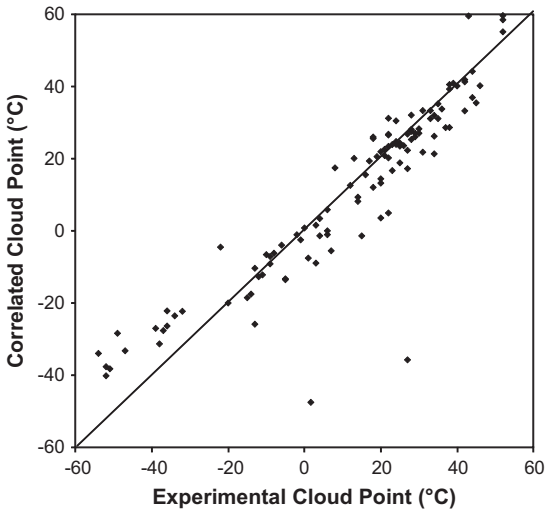

Fig. 4a. Parity plot for Cloud Point using linear correlation i.e. Eq. (7).

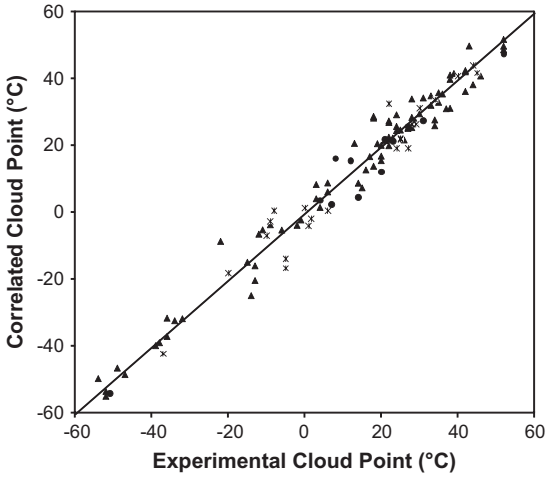

Fig. 4b. Parity plot for Cloud Point using ANN with weights corresponding to Table 4, training (▲), validation (∗) and testing datasets (•).

5.1. Pour Point correlations

Linear correlation for Pour Point is given below:

$$PP = -122.0996SG + 0.4125T_{10\%} + 0.2614T_{50\%} - 0.1774T_{90\%} - 40.0326 \quad (5)$$

Table 3b
Comparison of various correlations for Cloud Point.

Correlation	Specific gravity		MeABP (°C)		Cloud Point		Average absolute error (°C)
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	
API	0.7700	0.9300	171.29	407.41	−64.82	37.96	10.34
Linear	0.7883	0.9548	189.03	505.69	−54.00	52.00	6.48
ANN	0.7883	0.9548	189.03	505.69	−54.00	52.00	3.58

PP is the Pour Point in °C, SG is the specific gravity, $T_{10\%}$ is the distillation ASTM D86 – temperature in °C at 10% volume distilled, $T_{50\%}$ is the distillation ASTM D86 – temperature in °C at 50% volume distilled, $T_{90\%}$ is the distillation ASTM D86 – temperature in °C at 90% volume distilled.

Behavior of network has been shown in Figs. 1a and 1b. Reduction in the SSE with higher number of neurons in the hidden layer can be observed from Fig. 1a. However Mean Squared Error (MSE) and Shibata's Criterion (SC) increase after one neuron in the hidden layer which could be observed from Fig. 1b. Selection of the optimum network was done using the SC and MSE. Hence network with one neuron in the hidden layer i.e. 7 weights was found to be the optimum. The weights for the network are presented in Table 2a.

Fig. 2a shows the parity plot for linear correlation. Average absolute error using linear correlations is 5.75 °C. Fig. 2b shows parity plot for correlation developed using neural network; average absolute error using neural network is 3.88 °C. Significant reduction in the spread of the parity plot and average absolute error can be observed for correlation developed using ANN. For ANN, with only marginal increment in the number of weights and complexity has reduced the error significantly compared to linear correlation.

Consistency of the network can be observed from the parity plot in which training, validation and testing datasets evenly distributed around the diagonal line. A graph with more spread for testing/validation could have meant over-training of the network and a correlation that is not generic enough for our purpose.

Pour Point values were also estimated using API correlation proposed in 2B8.1 for the database discussed in Section 4 to compare the accuracy of the proposed model. Table 2b shows the comparison of proposed model with API correlations. A significant reduction in the error could be observed from the table. To compare the range of the correlation; mean average boiling point (MeABP) was estimated for our database and it has been compared with that used by API correlation in Table 2b. Similarly, ranges of specific gravity and Pour Point have also been shown for the comparison. It could be observed that the overall range of Pour Point covered by our database is much wider than that used by API.

5.2. Cloud Point correlations

Linear correlation for Cloud Point is given below:

$$CP = -267.5332SG + 0.1315T_{10\%} + 0.7837T_{50\%} - 0.4301T_{90\%} + 89.1003 \quad (7)$$

CP is the Cloud Point in °C, SG is the specific gravity, $T_{10\%}$ is the distillation ASTM D86 – temperature in °C at 10% volume distilled, $T_{50\%}$ is the distillation ASTM D86 – temperature in °C at 50% volume distilled, $T_{90\%}$ is the distillation ASTM D86 – temperature in °C at 90% volume distilled.

As discussed for Pour Point, a similar analysis of SSE, MSE, SC vs N is shown in Figs. 3a and 3b for Cloud Point. A network with four neurons in the hidden layer i.e. 25 weights was found to be optimum. The weights for the network are shown in Table 3a.

The spread of values for the three sets i.e. training, validation and testing are almost the same. Thus proposed network is generalized. Fig. 4a shows the parity plot for linear correlation. Average absolute error using linear correlations is 6.48 °C. Fig. 4b shows parity plot for correlation developed using neural networks; average absolute error using neural network is 3.56 °C. Significant reduction in the spread of the parity plot and average absolute error can be observed for correlation developed using ANN.

Table 3b shows the comparison of proposed correlations with API correlations for Cloud Point proposed in 2B12.1. A significant reduction in the error and wider range of inputs and outputs for the ANN based correlations can be observed.

Though the information in the correlations developed using ANNs is difficult to decode, it can be seen from the linear correlations that the Pour Point and Cloud Point have similar dependence on the chosen properties though the coefficients are different. This has a basis in the way these properties are defined. Pour Point and Cloud Point are a measure of the n-paraffin content of the fuel and thus show a similar dependency on the properties.

Both Pour Point and Cloud Point increase with the reduction in density. This is due to the fact that the reduction in density is an indication of increase in the lighter fractions rich in paraffins. Fractions rich in n-paraffinic components crystallize faster and have high Pour and Cloud Point. Sensitivity analysis done using ANNs has shown similar behavior with respect to density.

During the development of the proposed correlations initial and final boiling points were also used as inputs for the network which did not improve the accuracy of the network significantly. As these properties are not estimated accurately by simulators, they have not been used in the work. Similar to linear correlations, quadratic correlations were also developed. For Cloud Point the average absolute error for quadratic correlations was of the similar order compared to ANN however number of regression coefficients was higher i.e. 9 vis-à-vis 7 for ANN. Hence de-scaled SC for quadratic correlation was higher compared to that for ANN. Size of the network for Cloud Point is bigger than that for Pour Point. Due to this the number regression coefficients or weights for Cloud Point was higher for ANN based correlation compared to that of quadratic however reduction in the error was significant using ANNs. Based on the comparison of de-scaled SC, correlation based on ANN proved to be better than quadratic for Cloud Point as well.

6. Conclusions

Pour Point and Cloud Point are important parameters for a fuel especially the middle and heavy distillates. Therefore good correlations for the same are of significant importance. Linear and ANN based correlations have been proposed for Pour Point and Cloud Point of mixtures. Linear correlations are simple and easy to use however errors for these correlations are higher than ANN based. For Pour Point the best correlation was ANN with 7 weights and for Cloud Point, ANN with 25 weights. The linear correlation shows the dependency of Pour Point and Cloud Point with each of the chosen property from which we can also conclude the close relationship between these two. Also a robust correlation for both Pour

Point and Cloud Point was found in the form of ANN with an average absolute error of 3.77 °C and 3.58 °C, respectively. These correlations can be easily employed for property estimation based on user's requirements of performance or accuracy.

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References

[1] ASTM D97. Standard test method for pour point of petroleum products. Philadelphia: ASTM International; 2008.
[2] Chatterjee T, Saraf DN. On-line estimation of product properties for crude distillation units. J Process Control 2004;14:61–77.
[3] ASTM D2500. Standard test method for cloud point of petroleum products. Philadelphia: ASTM International; 2005.
[4] Coutinho JAP, Mirante F, Ribeiro JC, Sansot JM, Daridon JL. Cloud and pour points in fuel blends. Fuel 2002;81(7):963–7.
[5] Riazi MR, Daubert TE. Predicting flash and pour points. Hydrocarb Process 1987;66(9):81–3.
[6] Chakrabarti S. Estimation of properties for petroleum fractions using regression models. MTech. dissertation, I.I.T, Kanpur; 1997. [Cross Ref [2]].
[7] Ganguly S, Sadhukhan J, Saraf DN. Artificial neural network based estimation of petroleum and product properties. Ind Chem Eng Section A 2002;44:294–9 [Cross Ref. [2]].
[8] American Petroleum Institute (API). Technical data book—petroleum refining, 6th ed.; 1997.
[9] Claudy P, Letoffe JM, Neff B, Damin B. Diesel fuels: determination of onset crystallization temperature, pour point and filter plugging point by differential scanning calorimetry. correlation with standard test methods. Fuel 1986;65(6):861–4.
[10] Caswell KA, Glass TE, Swann M, Dorn HC. Rapid prediction of various physical properties for middle distillate fuels utilizing directly coupled liquid chromatography/proton nuclear magnetic resonance. Anal Chem 1989;61(3):206–11.
[11] Pasadakis N, Sourligas S, Foteinopoulos Ch. Prediction of the distillation profile and cold properties of diesel fuels using mid-IR spectroscopy and neural networks. Fuel 2006;85(7–8):1131–7.
[12] Cookson DJ, Iliopoulos P, Smith BE. Composition-property relations for jet and diesel fuels of variable boiling range. Fuel 1995;74(1):70–8.
[13] Zell A, Mamier G, Vogt M, Mache N, Döring S, Sommer T, et al. Stuttgart neural network simulator (SNNS version 4.2) IPVR, University of Stuttgart 1990–1995, and WSI, University of Tubingen 1990–1998.
[14] Tambe SS, Kulkarni BD, Deshpande PB. Elements of artificial neural networks with selected applications in chemical engineering, and chemical and biological sciences. USA: Simulation and Advances Controls, Inc.; 1996.