Correlation of Low Temperature Properties of Diesel fuel with Composition

R. Krishna, S. Bhattarcharjee, G. C. Joshi, H. Singh, R. C. Purohit, S. V. K. Dilawar, K. K. Singh

This work aims to find a correlation between the low temperature properties of diesel fuel (i.e. pour point [PPt], cloud point [CPt] and cold filter plugging point [CFPP]) and parameters such as ASTM mild-boiling temperature (T 50), wax content (WC), n-paraffin concentration (PC) and average n-paraffinic chain length (CL). Diesel fuel blends from different refinery streams derived from Bombay High Crude, along with the parent refinery streams, were characterised to determine their physico-chemical, cold-flow and compositional properties. Correlations were developed between the cold flow properties and the parameters: T 50, WC, PC, and CL. The results of this study should provide an aid to determining the optimum blending strategies in order to meet specifications with respect to the cold flow properties.

Das Ziel dieser Arbeit ist eine Korrelation zwischen den Tieftemperatur-Eigenschaften des Dieselkraftstoffes – d. h. Pour point (PPt), Cloud point (CPt), Cold filter plugging point (CFPP) – und den Parametern wie ASTM mid-boiling temperature (T 50), Vax content (WC) und average n-paraffinic chain length (CL). Die Ausgangskomponenten wurden aus dem Rohöl Bombey High erhalten. Die daraus zusammengesetzten Dieselqualitäten wurden nebst den Ausgangskomponenten untersucht und die physikochemischen Eigenschaften sowie die Kaltfließcharakteristiken ermittelt. Korrelationen zwischen den Kaltfließcharakteristiken und den Parametern T 50, WC, PC und CL wurden entwickelt. Die Ergebnisse dieser Studie dürften nützliche Hinweise bei der Ermittlung der optimalen Blending-Strategien geben, um den Spezifikationen hinsichtlich der Kaltfließ-Charakteristiken entsprechen zu können.

Introduction

Low temperature flow properties of distillate fuels such as pour point (PPt), cloud point (CPt) and CFPP are important considerations during their handling and their application in engines and other appliances. These cold flow properties are commonly believed to be primarily controlled by the *n*-paraffinic components of these fuels [1–5]. Upon cooling the distillate fuels, "wax" crystals, containing predominantly n-paraffins of the high chain lengths, separate out. These crystals may interlock forming a cage-like structure which entraps the liquid phase. At a certain stage the fuel flow ceases. Even if a percent or two of separated wax crystals are thus formed, cessation of free flow of the fuel may result [3]; the temperature at which this occurs is the pour point.

While there have been soma attempts to correlate one or other cold flow property with average molecular weight or n-paraffin content of the fuel [4–6], there appears to be no systematic study carried out to determine all the relevant independent paramaters. The object of tha present study was to develop a correlation after a systematic examination of the possible correlations. It was also tha objective of the exercise to provide an aid to refinery blending schames so as to meet the relevant cold flow property specification. To meat this latter aim the study was carried out with eight refinery streams, all derived from Bombay High Crude Oil, blended in twenty four different ways. The data generated on a detailed characterisation of the individual streams and their blends form the basis of the correlations and conclusions developed in this paper.

Experimental

Eight refinery streams were obtained from Bharat Petroleum Corporation Ltd., Bombay; thesa streams consisted of straight run products (e.g. kerosine, gas oils) and cracked stocks (light and heavy cycle oils) from a fluid catalytic cracking unit. All the eight refinery streams originated from the sama crude oil source, Bombay High, and are listed in *Table I*. These eight refinery streams were blended in twenty-four different ways and the two sets were characterised for:

- CPt, PPt and CFPP,
- density, viscosity and distillation characteristics,
- wax content and an estimate of urea adduct forming components,
- C-number distribution of n-paraffins in the urea adductable portion.

Standard IP/ASTM procedures were followed for cold flow tests and for other characteristics. Wax content was estimated using the Engler Holde procedure. C-number distribution was obtained by gas chromatography. Table I summarizes the properties of the eight refinery streams: a summary of the properties of the twenty four blends is to be found in *Table II*.

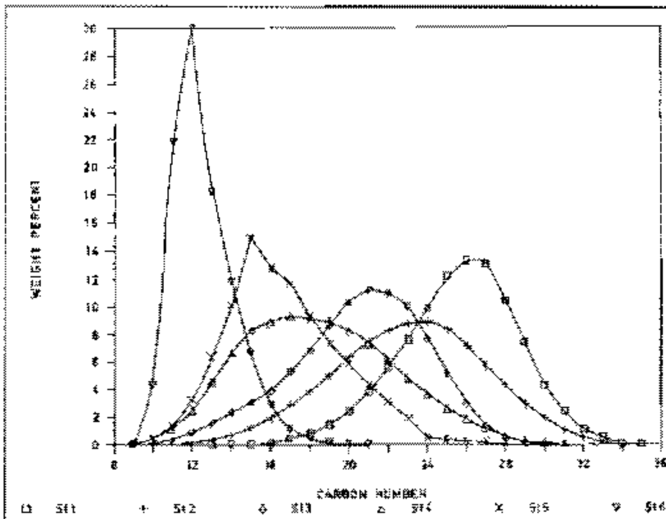

Figure 1: Carbon Number Distribution for n-Paraffins in various streams 1–8

zu Table II:

Stream identification:

Stream 1: HCO = Heavy Cycle Oil; Stream 2: Gas Oil IV + JBO; Stream 3: LCO = Light cycle oil; Stream 4: Gas oil III; Stream 5: Gas oil I; Stream 6: Kerosine; Stream 7: PFB = Prefactionator bottoms; Stream 8: Gas oil II

(*) Streams/blends marked with an asterisk were omitted from the correlation analysis.

Table I: Physio-Chemical Characteristics of Component Streams

Characteristics \ Stream No.	1	2	3	4	5	6	7	8
	HCO	GO IV + JBO	LCO	GO III	GO I	KERO	PFB	GO II
Density, gm/ml at 15 deg C	0.8688	0.8671	0.8571	0.8493	0.8405	0.8035	0.7872	0.8367
API gravity	31.28	31.60	33.45	35.02	36.77	44.52	46.17	39.52
Cloud point, deg C	47	43	8	22	4	–	–	–19
Pour point, deg C	39	39	6	18	0	–	–	–24
CFPP, deg C	38	33	7	16	–1	–	–	–21
Kin. viscosity, cSt at								
99 deg C	2.71	2.63	1.05	1.49	1.21	–	–	–
50 deg C	6.77	8.52	1.97	3.16	2.4	1.89	0.06	1.37
ASTM Distillation, deg C								
IBP	204	252	147	208	166	–	132	120
5% vol	294	285	188	238	217	–	137	149
10% vol	319	297	202	247	232	–	139	162
20% vol	339	315	221	259	249	–	142	180
30% vol	353	327	232	270	260	–	144	198
40% vol	383	340	245	280	267	–	147	213
50% vol	–	353	261	290	275	–	150	228
60% vol	–	366	280	303	283	–	153	241
70% vol	–	–	300	316	292	–	157	254
80% vol	–	–	320	334	304	–	163	267
90% vol	–	–	343	360	325	–	171	287
95% vol	–	–	362	–	346	–	180	307
FBP	–	–	–	–	359	–	191	321
Rec. up to 366 deg C	44	60	96.5	–	100	–	100	100
Wax content %wt (EH)	33.0	43.4	6.7	13.0	0.11	0.11	0.1	0.8
Aniline point, deg C	93.6	90.6	46.6	76.2	71.4	1.6	40.6	57.8
R.I. at 20 deg C	–	–	1.4949	1.4742	1.4695	1.4500	1.4400	1.4625
Diesel Index	62.71	61.64	39.72	60.62	80.74	–	–	58.94
Cetane Number	–	–	43	51	52	–	–	41
Urea adductables %wt	55.8	44.0	15.8	37.4	33.0	22.2	–	25.6

Table II: Properties of the Streams and Blends

Stream/ Blend	Compositions of streams 1–8 in various blends (%wt)								T50 ASTM Mid.b.p.	Cloud Point deg C	Pour Point deg C	CFPP deg C	WC %wt (EH)	PC %wt	CL Avg Chain Length
	Strm 1	Strm 2	Strm 3	Strm 4	Strm 5	Strm 6	Strm 7	Strm 8							
Stream 1	100.00								370	47	39	38	33.00	54.85	25.59
Stream 2		100.00							353	43	39	33	43.40	36.76	23.05
Stream 3			100.00						261	8	6	7	6.70	13.90	20.52
Stream 4				100.00					290	22	18	16	13.00	30.74	18.49
Stream 5					100.00				275	4	0	–1	0.11	24.12	16.70
Stream 6						100.00			–				0.11	2.58	12.54
Stream 7							100.00		150				0.10	2.60	12.56
Stream 8 (*)								100.00	228	–19	–24	–21	0.60	11.72	14.73
Blend A1	11.20	88.80							356	38	36	34	42.33	44.97	23.91
Blend A2	7.53	59.46	33.10						331	34	30	30	36.50	33.26	22.64
Blend A3	3.70	29.20	16.21	50.89					309	29	24	25	21.80	31.24	20.41
Blend A4	2.57	20.33	11.29	35.43	30.38				296	24	21	22	15.07	29.07	19.28
Blend A5	2.08	16.23	9.01	28.29	24.25	20.17			277	21	15	18	12.05	23.74	17.92
Blend A6	1.82	14.37	7.98	25.03	21.46	17.04	11.51		265	18	15	16	10.67	21.28	17.21
Blend a1						60.63	39.37		–				0.11	1.27	12.32
Blend a2 (*)					42.16	35.07	22.77		216	–8	–12	–15	0.11	9.47	15.33
Blend a3				32.93	26.28	23.52	15.27		250	7	3	1	4.35	16.10	16.89
Blend a4			9.60	29.77	25.57	21.26	13.80		250	7	3	3	4.57	16.46	17.27
Blend a5		14.53	8.21	25.44	21.85	18.17	11.80		263	18	9	11	10.21	20.37	17.23
Blend a6	1.80	14.27	8.05	24.96	21.46	17.64	11.60		262	19	15	16	10.62	24.22	18.59
Blend B1	11.24							88.76	239	15	9	13	4.20	17.37	17.77
Blend B2	7.53		33.01					59.46	243	12	8	10	5.05	15.72	18.24
Blend B3	3.70		16.21	50.89				29.20	272	15	9	14	9.10	22.53	18.10
Blend B4	2.57		11.29	35.43	30.37			20.33	273	12	9	11	6.30	19.36	18.39
Blend B5	2.06		9.01	28.28	24.25	20.17		16.23	258	10	3	8	5.10	21.62	17.42
Blend B6	1.82		7.98	25.03	21.46	17.82	11.51	14.36	246	9	3	6	5.30	11.88	17.60
Blend b1 (*)						60.63	39.37		–		–50		0.11	1.40	12.27
Blend b2 (*)					42.16	35.07	22.77		214	–8	–12	–15	0.11	12.32	15.44
Blend b3				32.93	28.18	23.52	15.27		246	8	3	1	4.35	12.44	17.36
Blend b4			9.60	29.77	25.57	21.26	13.80		246	8	3	1	4.57	17.42	16.92
Blend b5			8.21	25.44	21.85	18.17	11.80	14.53	247	6	–3	–1	4.00	16.58	17.21
Blend b6	1.60		8.08	24.96	21.46	17.84	11.59	14.27	248	8	0	4	4.52	16.96	17.17

Table III: Correlation Analysis of Cloud, Pour and CFPP with Mid Boiling Point, n-Paraffin Concentration, Wax Concentration and Average n-Paraffin Chain Length

Dependent variable Y	Independent X1	Variable X2	A0	A1	A2	R^2	Standard error in Y
CPT	T50		−64.7185	0.2972		0.8738	4.3945
CPT	PC		−7.7211	1.0671		0.8504	4.7842
CPT	CL		−66.1032	4.4388		0.8013	5.5134
CPT	WC		6.1774	0.9081		0.8915	4.0745
CPT	LOG(T50)		−474.2950	201.9293		0.9140	4.6047
CPT	LOG(WC)		−14.0616	33.2645		0.9196	4.4863
CPT	LOG(PC)		−68.2183	63.9751		0.8032	5.4869
CPT	LOG(CL)		−247.4200	208.2902		0.8003	5.5266
CPT	PC	CL	−34.6991	0.6798	1.9177	0.8879	4.2337
CPT	T50	WC	−24.9724	0.1291	0.5410	0.9108	4.7779
CPT	T50	CL	−67.5799	0.2302	1.1355	0.8818	4.3476
CPT	CL	WC	−11.2104	1.0449	0.7237	0.8992	4.0161
CPT	PC	T50	−48.0719	0.3796	0.1974	0.8829	4.3287
PPT	T50		−72.9637	0.3086		0.8857	4.3135
PPT	PC		−13.2469	1.0858		0.8277	5.2957
PPT	CL		−74.3374	4.6059		0.8111	5.5457
PPT	WC		0.6521	0.9432		0.9042	3.9496
PPT	LOG(T50)		−500.1610	210.4323		0.9221	3.5592
PPT	LOG(WC)		−20.7515	34.8754		0.9390	3.1497
PPT	LOG(PC)		−75.3956	65.5372		0.7924	5.8132
PPT	LOG(CL)		−263.5550	216.9762		0.8164	5.4662
PPT	PC	CL	−45.6965	0.6199	2.3066	0.8788	4.5419
PPT	T50	WC	−31.5202	0.1334	0.5641	0.9235	4.6061
PPT	T50	CL	−75.8793	0.2404	1.1571	0.8935	4.2561
PPT	CL	WC	−16.9541	1.0580	0.7566	0.9116	4.8794
PPT	PC	T50	−66.5746	0.1301	0.2744	0.8867	4.3911
CPPP	T50		−62.0070	0.2721		0.8159	5.0299
CPPP	PC		−9.7410	0.9739		0.7888	5.3871
CPPP	CL		−64.8525	4.1479		0.7793	5.6066
CPPP	WC		2.8667	0.8347		0.8389	4.7048
CPPP	LOG(PC)		−66.1722	59.2934		0.7684	5.8406
CPPP	LOG(CL)		−236.0750	196.0450		0.7697	5.3759
CPPP	LOG(T50)		−439.132	185.7662		0.8740	4.1048
CPPP	LOG(WC)		−16.2560	31.1911		0.9133	4.4051
CPPP	PC	CL	−39.8013	0.5423	2.1358	0.8406	4.7837
CPPP	T50	WC	−23.5751	0.1096	0.5231	0.8544	4.5735
CPPP	T50	CL	−65.9985	0.1787	1.5841	0.8333	4.8931
CPPP	CL	WC	−19.6400	1.3525	0.5961	0.8532	4.5917
CPPP	PC	T50	−46.6211	0.3093	0.1908	0.8225	5.0484

Results and Discussion

The C-number distribution of the n-paraffins present in the individual refinery streams have been plotted in *Figure 1*. It is observed that the distribution is gaussian in form but skewed. As one passes from a higher boiling stream to a lower boiling one, the asymmetry of the C-number distribution shifts from right (higher carbon number) to left (lower carbon numbers). From the C-number distribution the average chain length of the n-paraffins, CL, can be calculated and the values for the various streams and blends are given in *Table II*. Further it is to be expected that the low temperature flow properties of any stream will not be affected by the n-paraffin molecules shorter than 15 in chain length [7]. With this in mind we have also listed in *Table II* the concentration of n-paraffins, in % wt, having a chain length longer than 15; we shall denote this variable as PC.

Before proceeding to determine the appropriate correlations, an attempt was made to determine the important parameters which would affect the cold flow properties and to see whether there was any interdependence between these parameters. By plotting PC, CL, WC and T 50 against one another, an interrelationship between these variables was established, which is in agreement with an earlier work, e.g. *Knepper* and *Hutton* [4]. Some of these dependences are shown in *Figures 2–4*. It is therefore concluded that a correlation can be sought between each cold flow property and any one of the four parameters PC, CL, WC and T 50 or a combination of these parameters.

Let Y represent any cold flow property (CPt, PPt or CFPP) and X1 and X2 denote any combination of the independent variables PC, CL, WC or T 50 or the logarithmic of these variables. Correlations of the form:

$$Y = A0 + A1 \times X1 + A2 \times X2 \quad (1)$$

were obtained by linear regression. The results of the studies are presented in *Table III*, which also lists the R^2 of these correlations along with the standard error in the Y-estimate. An examination of the *Table III* shows that the best correlations are obtained between the cold flow property and log (WC); the standard error in the estimate of any cold flow property is within 3.5 °C, which is about the order of repeatability of the determinations of these cold flow properties. It is indeed remarkable that log (WC), on its own, performs better than multi-variable correlations. *Figures 5–7* show the best correlations obtained.

The foregoing studies are with refinery streams originating from Bombay High Crude Oil; with other crudes the relationship coned be expected to be similar, however, with other values of the coefficients A0, A1 and A2.

Conclusions

From a detailed characterization of eight refinery streams and twenty-four blends of these streams some insights have been gained on the relationship between cold flow properties CPt, PPt and CFPP and "independent" parameters: PC, CL, WC and T 50. The best correlation was observed between any cold flow

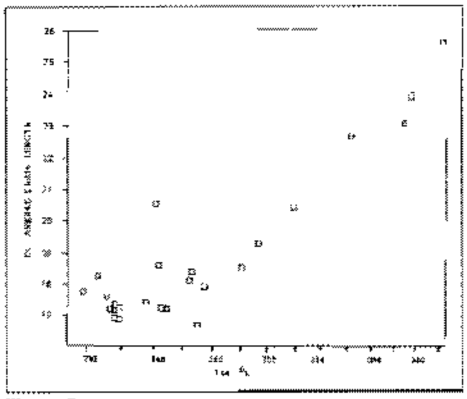

Figure 2

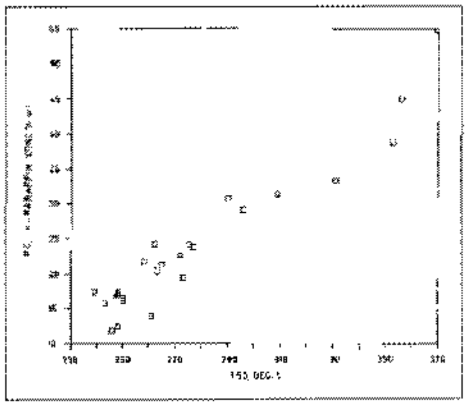

Figure 3

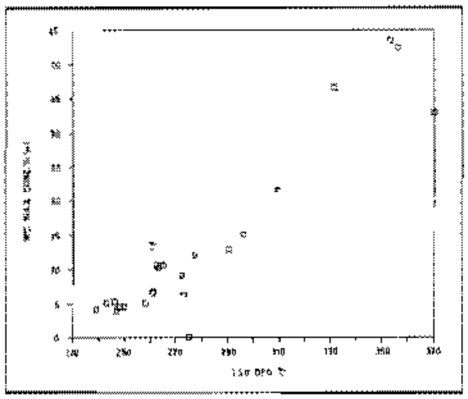

Figure 4

Figure 2: Interdependence between average n-paraffinic chain length CL and the ASTM mid boiling temperature, T50
Figure 3: Interdependence between PC, n-paraffinic concentration, and the ASTM mid boiling temperature, T50
Figure 4: Interdependence between WC, wax concentration, and the ASTM mid boiling temperature, T50
Figure 5: Correlation between cloud point and log (wax concentration)
Figure 6: Correlation between pour point and log (wax concentration)
Figure 7: Correlation between CFPP and log (wax concentration)

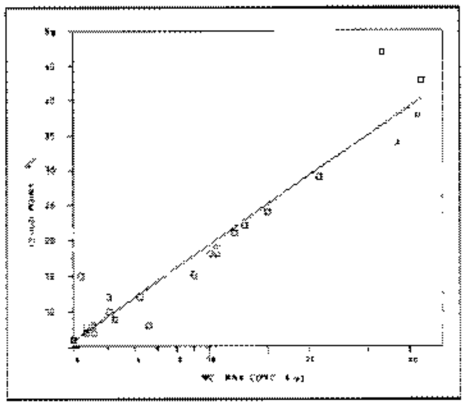

Figure 5

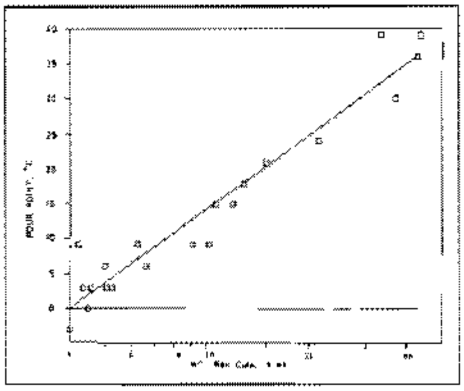

Figure 6

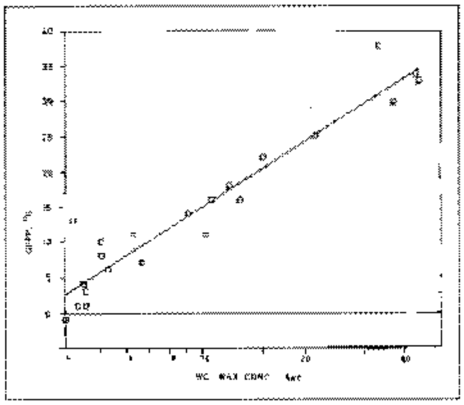

Figure 7

property and log (WC), where in the estimates were of the order of accuracy of the experimentation.

The results of this study though quantitatively valid for streams of Bombay High Crude origin, should provide guidelines for obtaining correlations for other crudes as well. Also, the results could be used to develop optimum blending strategies to meet desired specifications of the cold flow properties.

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References

[1] *W. R. Turner:* **Ind. Eng. Chem. Prod. Res. Dev.**, 10 (3), 238 (1971)
[2] *F. J. Pass, Ch. Csokuch, K. Wastl*, **7th World Petroleum Congress**, Vol 8, p. 129 (1967)
[3] *L. I. Rossamyr:* **Ind. Eng. Chem. Prod. Res. Dev.**, 18 (3), 227 (1979)
[4] *J. I. Knepper, R. P. Hutton:* **Hydrocarbon Processing**, 54 (9), 129 (1975)
[5] *J. Hu, A. M. Burns:* Hydrocarbon Processing, 49 (11), 213 (1970)
[6] *M. R. Riazi, T. E. Daubert:* **Hydrocarbon Processing**, 66 (9), 81 (1987)
[7] *S. R. Reddy, M. L. McMillan:* SAE Paper 811181 (1982)

Nomenclature

Stream 1 = HCO = Heavy Cycle Oil
Stream 2 = Gas Oil IV + JBO (Jute Batching Oil)
Stream 3 = LCO = Light Cycle Oil
Stream 4 = Gas Oil III
Stream 5 = Gas Oil I
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CPt = Cloud Point, °C
PPt = Pour Point, °C
CFPP = Cold Filter Plugging Point, °C
PC = %wt of n-paraffins having chain length longer than 15
CL = average n-paraffinic chain length
WC = % wt wax concentration, determined by Engler-Holde method
Y = any cold flow property, °C
X1, X2 = independent variables in correlation