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Research on the Rate Prediction Model of Diesel Oxidation in Storage

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The existent gum of five diesel samples under five different partial pressure of oxygen (PPO) (21%, 15%, 10%, 5%, 1%) was investigated by means of storage test method. The formation rate of existent gum (K) was established by the least square method. The influence of diesel composition and partial pressure of oxygen on K is examined. Multiple linear regression method and least square method were carried out to establish two models to predict the existent gum formation rate. Results indicate that existent gum increases linearly with the storage time during oxidation reaction. The reaction of olefin and oxygen is the main one of forming existent gum. The relationship between K and PPO is power function, mass fraction of olefin has a linear effect on K. F test results proved the correctness of the diesel oxidation model, which can be used to predict the diesel oxidation.

1. Introduction

How to precisely predict the storage stability of liquid fuel is one of the problems haunted the fuel workers for a long time. Both fuel composition and external conditions exerts great influences on the fuel stability (Xu et al., 2010). The good prediction model should be grounded on the fundamental knowledge of all factors that contribute to the degradation of fuel, which includes the intrinsic factors such as unsaturated hydrocarbons (Lin et al., 2012; Ren et al., 2012), nitrogen-containing compound, oxygen-containing compound and sulfur - containing compound (Joanna et al., 1987; Isabelle et al., 1999; Mushrush et al., 1991) as well as external conditions such as light, temperature and the presence of metals (Batta et al., 1991; Wu et al., 2008). Little work has been done to consider the influence of external oxygen especially the lower oxygen partial pressure. Furthermore, present researches mainly focus on qualitative descriptions rather than quantitative model establishment. Existent gum amounts were chosen as indicators of the degree of oxidation of different diesel fuels, which were aged under different oxygen partial pressures, the mathematical relationship between diesel composition, oxygen partial pressure and diesel oxidation rate was established, which provides a theoretical basis for predicting the oxidative deterioration rate of diesel.

2. Materials and Methods

2.1 Fuel samples

Two kinds of 0# automobile diesel samples (numbered SH1 and SH2) were obtained from Sinopec Chongqing Branch Corporation, two kinds of 0# ordinary diesel samples (numbered SY1 and SY2) from PetroChina Chongqing Branch Corporation, and one kind of military diesel sample (numbered PB1) from PingBa depot. The Physical and chemical properties of diesel samples were summarized in Table 1.

2.2 Qualitation and quantification of diesel by GC/MS

The components of diesel samples were determined using a gas chromatograph mass spectrometer (GC7890A/MS5975C, Agilent). The column was capillary column (HP-1MS; 30m × 250 μm × 0.25 μm). Operating conditions were as following: ultra-high purity helium was used as the carrier gas at a flow rate of 1.0 mL min-1 and analyses were performed in constant flow mode while the injector temperature was set at 340°C for split injection at a split ratio of 10:1. The inject volume was 1 μL. The initial oven temperature was maintained at 100 °C for 1 min before it was increased by 5 °C min−1 to 300 °C and kept isothermal for 5 min.

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The ionization potential of the mass-selective detector was 70 eV and the scan range was 30–650 u. Identification of compounds were achieved by a mass spectra database search (NIST05 Library) and co-eluted with corresponding standards. Peak area normalization method was used in order to obtain the mass fraction of each component. The results were shown in Table 2.

Table 1: Physical and chemical properties of diesel samples

Item	Distillation temperature/℃			Existent gum	Acidity	Colority
	50%	90%	95%	mg/100ml		level
SH1	260	332	340	19.2	1.59	7
Item	Distillation temperature/℃			Existent gum	Acidity	Colority
	50%	90%	95%	mg/100ml		level
SH2	280	340	355	42.0	2.99	3
SY1	266	334	350	79.0	3.24	11.5
SY2	275	345	360	31.3	2.64	6
PB1	233	295	310	13.2	1.36	6

Table 2: Component of diesel samples

Component w%	SH1	SH2	SY1	SY2	PB1
Paraffin	62.27	56.22	61.34	55.87	50.75
Cycloparaffin	5.77	6.82	8.04	6.77	11.91
Benzene	6.70	5.71	2.98	6.67	1.31
Naphthalane	10.44	10.01	10.06	9.79	18.39
Tricyclic aromatics	0.83	0.49	2.46	1.48	1.12
Non-Conjugated diene	4.98	8.20	7.86	9.28	4.69
Conjugated diene	0	2.54	0.58	2.14	0.04
Oxygen-containing compounds	8.16	7.02	6.03	6.06	8.53
Nitrogen-containing compounds	0.62	1.59	0	1.72	0.94
Sulfur-containing compounds	0.23	1.40	0.65	1.25	2.32

2.3 Storage test

5L of diesel was taken and poured into five 1L beakers, which were later placed within five apparatuses, and the temperature of all the apparatus was set at 95℃. Then, the apparatus was filled with one atmosphere air first and then slowly purged with nitrogen to decrease the oxygen content in the air to obtain five different oxygen partial pressures, 21%, 15%, 10%, 5%, 1%. Regular supply of oxygen into the apparatus was needed later to maintain the oxygen partial pressure at the set value. 100ml sample was taken periodically with 4mm valve inserted into the device. Test apparatus is shown in Figure 1.For diesel samples taken periodically during the storage test process, their existent gum was measured according to GB / T509 "Determination of engine fuel existent gum".

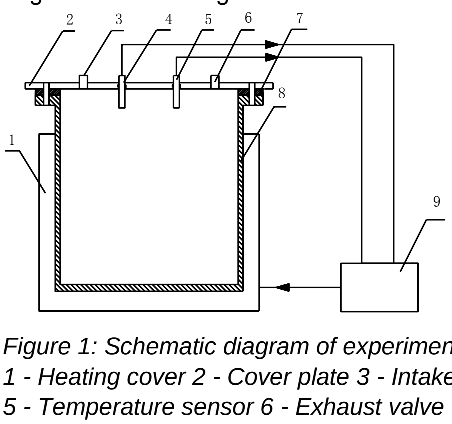

Figure 1: Schematic diagram of experimental unit
1 - Heating cover 2 - Cover plate 3 - Intake valve 4 - Oxygen sensor
5 - Temperature sensor 6 - Exhaust valve 7 - Seal ring 8 - Tool housing 9 - Controller

3. Results and discussions

3.1 Existent gum results

The existent gum results of diesel samples were summarized in figure2~figure6.

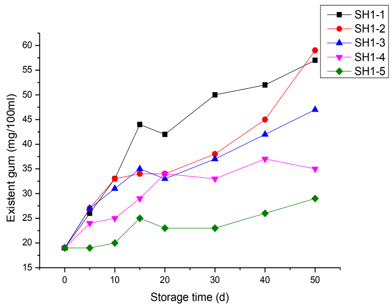

Figure 2: Dotted lines of SH1 samples

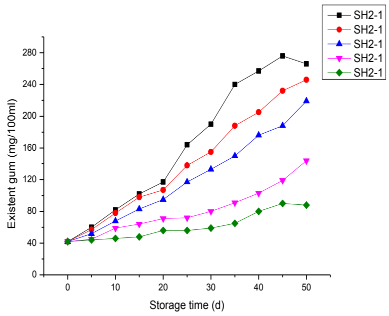

Figure 3: Dotted lines of SH2 samples

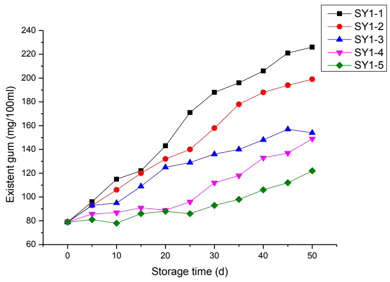

Figure 4: Dotted lines of SY1 samples

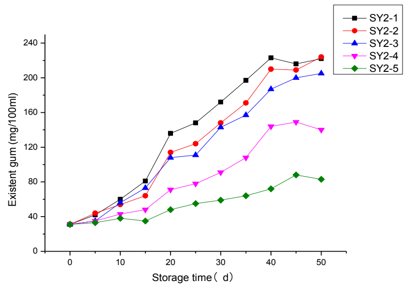

Figure 5: Dotted lines of SY2 samples

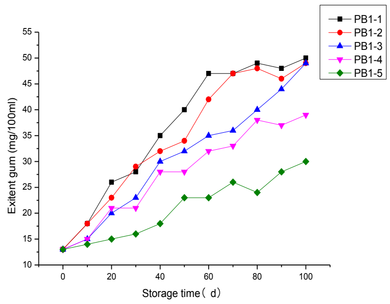

Figure 6: Dotted lines of PB1samples

3.2 Relationship between existent gum and storage time

The existent gum was usually preferred as an indicator for diesel storage stability, which increased linearly with storage time as can be seen from figure 2 to 6. It is assumed that the existent gum S (mg / 100ml) and the storage time t (d) exists a linear relationship during the oxidation reaction process as follows:

$$S=Kt+c0 \quad (1)$$

S is the existent gum (mg/100ml), K is a diesel gum growth rate (mg • $(100ml • d)^{-1}$), t is the storage time (d), c_0 is the intercept.

The least squares method is used to carry linear fit between existent gum and storage time for 5 groups of diesel fuels. The slope of the fitted line K, intercept c_0, F value are listed in Table 3. $F_{0.95}$ (1,9) is 5.12, it is can be seen F value of all diesel samples is greater than the $F_{0.95}$ (1,9), so at the 95% confidence level F test is significant, oxidation reaction process established linear relationship between existent gum and storage time.

Table 3: K,c_0,F of regression equation

Item	K	c_0	F	Item	K	c_0	F
SH1-1	0.7140	25.20	44.15	SY1-1	3.0927	82.95	469.21
SH1-2	0.6567	22.16	70.01	SY1-2	2.5320	80.99	772.53
SH1-3	0.4731	23.82	59.24	SY1-3	1.5691	84.86	223.79
SH1-4	0.3228	22.64	23.33	SY1-4	1.3996	71.99	111.91
SH1-5	0.2473	18.86	39.08	SY1-5	0.8218	73.00	74.81
SH2-1	5.2127	36.68	458.88	SY2-1	5.0800	19.51	394.25
SH2-2	4.3272	28.81	899.11	SY2-2	4.2564	20.22	387.27
SH2-3	3.6545	27.09	316.45	SY2-3	3.8655	22.09	637.16
SH2-4	2.0436	34.27	129.97	SY2-4	2.6254	19.63	169.85
SH2-5	1.0363	35.54	199.73	SY2-5	1.1836	25.51	169.82
PB1-1	0.5536	12.96	558.72				
PB1-2	0.4691	13.33	483.09				
PB1-3	0.3518	13.04	644.62				
PB1-4	0.2700	14.22	223.56				
PB1-5	0.1891	11.91	232.32				

3.3 Relationship between existent gum and diesel component

In order to determine which component in diesel has great influence on K, the linear correlation analysis was carried between regression equation K and chemical composition based on Table 2 and Table 3. Correlation coefficient obtained was summarized in Table 4.

Table 4: Correlation coefficient of K with component of diesel samples

Component \ PPO(0.1MP)	0.21	0.15	0.10	0.05	0.01
Alkane	-0.49948	-0.50749	-0.62016	-0.37546	-0.43860
Aromatic	-0.42318	-0.41416	-0.28326	-0.35154	-0.42109
Olefin	0.98756	0.98846	0.98005	0.99690	0.99267
Oxygen-containing compounds	-0.79560	-0.79051	-0.71448	-0.78563	-0.88599
Nitrogen-containing compounds	0.58011	0.59129	0.70968	0.54322	0.48506
Sulfur-containing compounds	-0.00514	-0.0083	0.04555	-0.58248	-0.05032

As can be seen, under different PPO, K and olefin content is positively correlated, and there is a higher correlation coefficient (0.98) between olefin content and K. So it is assumed that a linear relationship may exist between them.

3.4 Relationship between K and PPO

SPSS (18.0, IBM) software was used to perform curve estimation of K and oxygen partial pressure listed in Table 3, the power function model (2) was found as a fitting function which converges and was more consistent with the actual situation.

K=a1xb (2)

a_1 is a coefficient (mg $(100ml)^{-1}$ d^{-1} $(0.1MPa)^{-b}$), b is oxygen pressure reaction order, x is the PPO (0.1MPa).

Table 5: The fitting equation of relationship between PPO and K

Item	Fitting equation	R^2
SH1	$K= 1.4031x^{0.4359}$	0.9223
SH2	$K=12.8504x^{0.5729}$	0.9845
SY1	$K= 6.8983x^{0.5435}$	0.8978
SY2	$K=10.4060x^{0.4565}$	0.9891
PB1	$K= 1.0393x^{0.4380}$	0.8683

Fitting equation and R^2 are listed in Table 5. The model above can reflect the relationship between K and PPO more accurately.as R^2 is larger. The value of coefficient b was around 0.5 and quite similar for different fitting equations. So suppose PPO on the different components of the diesel oxidation reactions share the same reaction order, the power function model was corrected to model (3).

K=a2x0.5 (3)

The results in Table 6 were fitted according to model (3). The corrected power function model (4) has a better correlation between K and x. It was proved that the hypothesis is true, the reaction order of oxygen on different diesel is 0.5.

Table 6: Corrected fitting equation

Item	Fitting equation	R^2
SH1	$K= 1.5958x^{0.5}$	0.9312
SH2	$K=11.1114x^{0.5}$	0.9795
SY1	$K= 6.3254x^{0.5}$	0.9203
SY2	$K=11.3543x^{0.5}$	0.9870
PB1	$K= 1.1771x^{0.5}$	0.8922

3.5 Establishment of oxidation model

As has been discussed in section 3.4, there is only one coefficient a_2 in corrected model (3), and a_2 is quite different in different types of diesel. Olefin is the main reason for promoting existent gum, and when the PPO is constant, there exists a linear relationship between k and mass fraction of olefin in diesel. It is assumed that in the model (3), a_2 was determined by olefin content in diesel. So the oxidation model (4) was proposed. In the model, a_2= f(x), x is the mass fraction of olefin.

K= f(x)P0.5 (4)

Among these unsaturated hydrocarbons, conjugated diene is the most active one. If diesel contains a small amount of conjugated diene, diesel will be oxide to form existent gum easily (Mo et al 2002). Therefore, olefin in diesel is divided into conjugated diene and non-conjugated diene, a_2 is determined by two olefins content. Four types of diesel, SH1, SH2, SY1, PB1 were chosen to set up oxidation model. Non-conjugated dienes (x_1) and conjugated dienes (x_2) were independent variables while coefficient of a_2 is dependent variable.

a2=a3x1+ a4x2+c2 (5)

By using multiple linear regression analysis, equation (5) was worked out, and binary linear regression equation (6) was got.

a2= -4.556+1.222x1+2.223 x2 (6)

The R^2 of the fitting equation (6) is 0.999, the model (7) is got by plugging the equation (6) into equation (4).

K=(-4.556+1.222x1+2.223 x2)P0.5 (7)

Equation (7) is the diesel oxidation rate model, which is in terms of non-conjugated dienes and conjugated dienes in diesel. The model shows that the conjugated diene is indeed more active, its oxidation rate is approximately 1.8 times of the non-conjugated diene reaction rate.

3.6 Model verification

Diesel sample SY2, which was not included in oxidation model was used for establishing model verification. Model (7) was applied to predict the oxidation rate of SY2. Experimental values (Exp) and predicted values (Pre) and their relative error (R) are listed in Table7. The relative error of model (8) is below 6%, in which GB / T509 requires the relative error below 15%.

The correlation coefficient (r), and F test were calculated based on experimental and predicted values. r, F value and F test of $F_{0.95}$ (r-1, n-r) are listed in Table 8. F value is greater than the $F_{0.95}$ (1, n-2), so at the 95% confidence level F test is significant. The model can predict the oxidation accurately.

Table 7: Comparison of experimented and calculated result for K

Sample	PPO(0.1MPa)	Exp	Pre	R
SY2	0.21	5.0800	5.2958	4.25%
	0.15	4.2564	4.4752	5.14%
	0.10	3.8655	3.6546	5.45%
	0.05	2.6254	2.5843	1.56%
	0.01	1.1836	1.1558	2.34%

Table 8: r,F of the regression model

Item	r	F	$F_{0.95}$ (1, 3)
Model	0.995	297.74	10.13

4. Conclusions

Existent gum increases linearly with storage time. The main oxidation reaction in diesel is between olefin and oxygen, and oxidation rate of conjugated diene is approximately 1.8 times of the non-conjugated diene reaction rate. There is a power function between K and PPO, in which the reaction order is 0.5. F test results proved the correctness of the diesel oxidation model, and it's relative error is below 6%.

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