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Asphalt Binder Laboratory Short-Term Aging

Hamzeh Haghshenas

Robert C. Rea

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Nebraska Department of Transportation

Materials and Research - Flexible Pavements and Quality Assurance Section

Hamzeh F. Haghshenas, Ph.D.

Materials and Research Engineer

Nebraska Department of Transportation

Email: hamzeh.haghshenas@nebraska.gov

Robert C. Rea, P.E.

Assistant Materials and Research Engineer

Nebraska Department of Transportation

Email: robert.rea@nebraska.gov

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Hamzeh F. Haghshenas, Ph.D.
Materials and Research Engineer
Nebraska Department of Transportation
Email: hamzeh.haghshenas@nebraska.gov

Robert C. Rea, P.E.
Assistant Materials and Research Engineer
Nebraska Department of Transportation
Email: robert.rea@nebraska.gov

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The Rolling Thin Film Oven (RTFO) is widely used to simulate asphalt binder short-term aging. However, there is a general interest to improve the current short-term aging protocol especially for reducing the aging time. Besides, there are some doubts about the capability of RTFO in the simulation of aging of highly polymer modified asphalt binders which is mainly due to improper dispersion of such binders in the bottles during rotating and creeping of highly viscous binder out of the bottles during rotation. This work addresses the effect of time, temperature, airflow rate, and weight of asphalt binder on the laboratory short-term aging of asphalt binders and proposes an alternative protocol that can reduce the aging time and resolve some of the current short-term aging protocol shortcomings. In the first part of this study, two asphalt binders, from different sources, were examined in RTFO at different combinations of the above-mentioned test parameters. The high-end continuous performance grading temperature (estimated by dynamic shear rheometer), and carbonyl index (estimated by Fourier transform infrared spectroscopy) were considered as the two responses for quantification and qualification of laboratory aging. The statistical analysis showed that the first order terms of time, temperature, and weight as well as their interactive terms were statistically significant. However, the effect of airflow rate, within the studied range, was insignificant. Based on the findings of the first part of study, an alternative protocol was proposed for the study of short-term aging in a RTFO. One unmodified and three highly modified binders were aged in a RTFO under the current and proposed aging conditions for comparative purposes. According to the obtained rheological (high- and low-end continuous performance grading temperature and viscosity) properties as well as the chemical characteristics (carbonyl index, saturate-aromatic-resin-asphaltene fractions, and oxygen content), it was shown that the proposed laboratory short-term aging protocol not only can reduce the aging time of the conventional protocol, but also that it is applicable to both neat and polymer-modified modern asphalt binders.

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Chapter 1. Introduction and Background

Appropriate simulation of the field aging process of asphalt binder, for the prediction of rheological/mechanical and chemical properties of this viscoelastic material, by employing the laboratory protocols, is a prerequisite for their successful commercial exploitation. This is especially crucial when this process (aging) is in direct relationship with durability of asphalt mixtures [1-4] and results in an increase in the stiffness [5] and a decrease in the cracking resistance [6]. Typically, the aging process is initiated from the asphalt mixture production step, and it is continued during the service life of asphalt mixtures [7, 8]. When hot asphalt binder and aggregates are blending, and then being transported and layed into pavement mat, the asphalt binder experiences hardening due to the loss of volatiles and/or oxidation; this process is called “short-term aging”.

Rolling Thin Film Oven (RTFO) protocol is currently available and widely used in the United States [9]; this protocol was introduced in the 1960’s and accepted by ASTM in 1970 [10]. In the Strategic Highway Research Program (SHRP), RTFO was implemented for the prediction of short-term oxidative aging during creation of hot-mix asphaltic concrete, and laydown mat placement. In a typical RTFO protocol [9], 35 grams of binder is poured into the bottle in a rotating carriage; it is then subjected to air with a flow rate of 4 liters/minutes (4000 milliliters/minutes) for 85 minutes at 163°C. It is assumed that a film of asphalt binder is continuously exposed to heat and air similar to the conditions experienced in the production of hot mix asphalt. Although the real conditions in the production of hot mix asphalt cannot be reproduced in RTFO, the results of numerous experiences indicate that the level of oxidative aging is adequately consistent with what occurs during the continuous-feed mixing drum plant sites [10]. This means that the changes in chemical and mechanical properties that occur during real conditions can be reliably predicted by employing RTFO protocol.

Although it is reported that the RTFO can adequately simulate the short-term aging, the current RTFO protocol is inefficient in the simulation of highly viscous binders (the polymer modified asphalt binders and performance grade (PG) 70-XX and higher) due to improper dispersion throughout the bottles and creeping of highly viscous binder out of the bottles during rotation [11, 12]. In addition, there are some doubts about the capability of RTFO in the simulation of the oxidative aging process that occurs during warm mix asphalt (WMA) production [13, 14]. There are some efforts to improve the current short-term aging protocol. For instance, researchers in Europe have recently examined the effect of different aging temperatures on properties of short-term aged WMA binders [15-17]. They reported that the degree of aging which occurs in the production of WMA mixture is lower than that of aged through RTFOT at 163 °C [13, 14] and therefore the current recommended temperature in RTFO protocol (i.e., 163 °C) should be decreased for more accurate simulation of aging in a WMA mixture. On the other hand, Bahia et al. [12] proposed and studied two modifications in RTFO test procedure to resolve the improper dispersion of highly modified binder throughout the bottles. They introduced steel spheres and steel rods to create a film of asphalt binder during the aging process. They reported that the steel rods can improve dispersion of highly modified binders better than steel spheres [12]. However, the results of a research carried out by the Federal Highway Administration (FHWA) and the Southeast Asphalt User Producer Group showed that the level of aging occurs in modified RTFO by steel rods is lower than that of happens for modified and unmodified asphalt binders during short-term aging in the field. In addition, this modification resulted in a spillage issue for both types of binders (i.e., modified and unmodified) [18].

A survey on previous literature indicates that the effects of time and temperature have been in the center of attention in the study of short-term oxidative aging [19, 20]. However, the proper choice of the value of short-term aging parameters is necessary for a successful simulation of a short-term aging process, especially when these parameters can be influenced by the other parameters (i.e. the interactions). By the use of Design of Experiments (DOE) strategies, such as Response Surface Methodology (RSM) based on Central Composite Design (CCD), some important information about the interactions can be acquired [21-23]. This information may result in new levels of RTFO parameters (new/alternative protocol); including time, temperature, airflow and weight of binder poured in RTFO bottles. However, any new/alternative protocol should be able to address the concerns about the conventional RTFO regarding the aging of neat (unmodified) binders and modified binders.

1.1 Objectives

The objective of this study was to statistically investigate the effect of time, temperature, airflow rate, and asphalt binder weight on the chemical and rheological properties of different asphalt binders in the laboratory short-term aging (RTFO) process. Based on the results and findings of statistical analysis, it was attempted to propose an improved RTFO aging protocol, which was applicable on both unmodified and highly modified binders, without affecting the extent of aging compared to the current standard procedure.

1.2 Methodology

This study was designed and performed in two phases. In phase 1, it was attempted to investigate the effect of time, temperature, airflow, and asphalt binder weight on the laboratory short-term aging (RTFO) and propose an alternative laboratory aging protocol for simulation of short-term aging process. This protocol was then validated in phase 2 of the project to determine its applicability for different types of binders, including one unmodified and three highly modified ones. To accomplish this, the binders were aged in laboratories of the Nebraska, Kansas, and Iowa Department of Transportation (DOT) under both the current and the alternative standard. Then the rheological properties (i.e., high-end and low-end asphalt binder PG and viscosity), and chemical characteristics (i.e., saturate-aromatic-resin-asphaltene (SARA) analysis, Fourier-transform infrared (FT-IR) spectroscopy, and elemental (carbon, nitrogen, hydrogen, sulfur and oxygen) analysis) of aged binders were measured. It should be noted that only the samples aged in Nebraska DOT were used for chemical analysis. This chemo-physical approach was intended to show whether or not the alternative protocol results are in a similar aging process as the current protocol. The schematic diagram of the experiments conducted in present study was illustrated Figure 1.

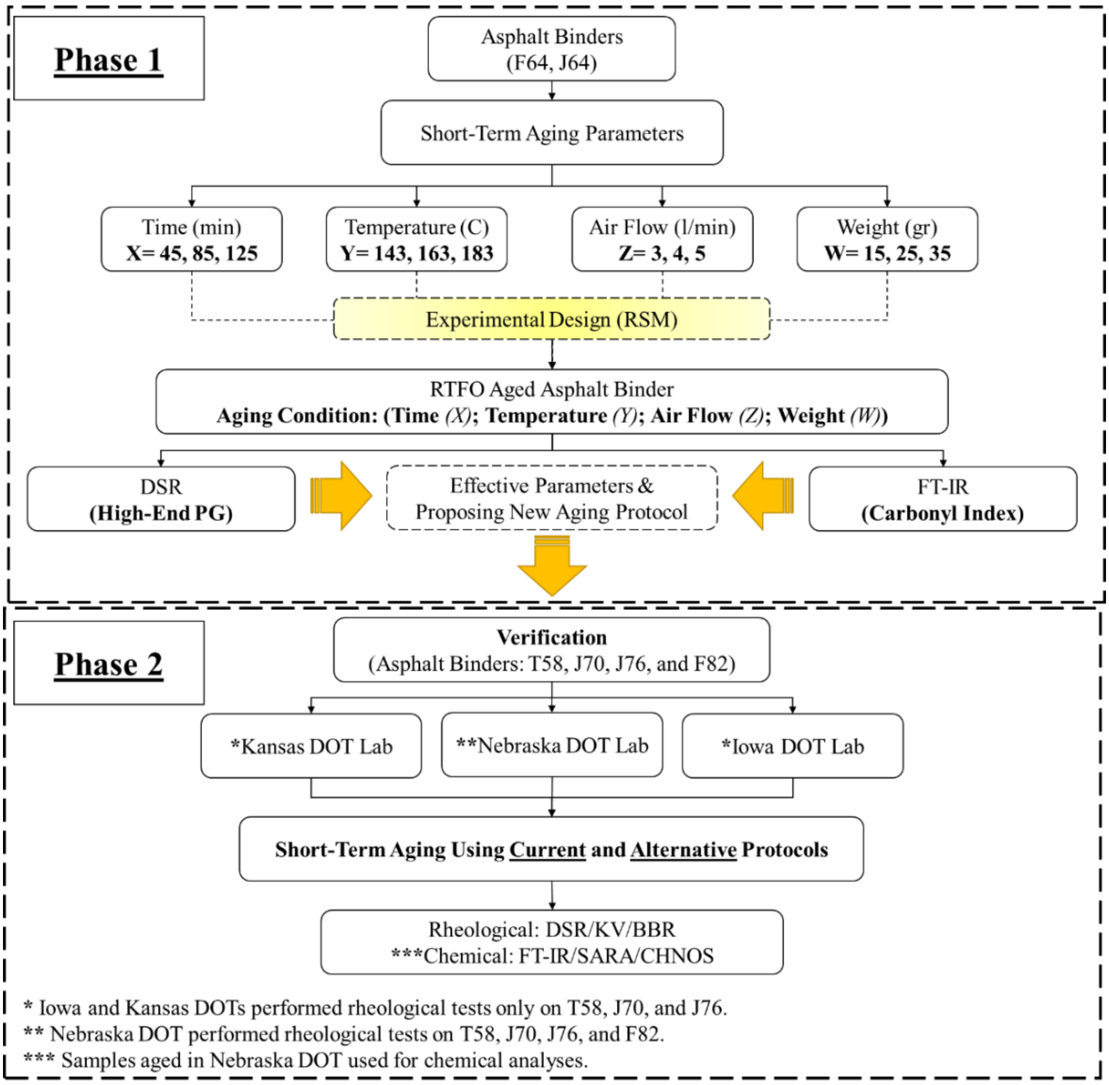


Figure 1. Schematic diagram of the conducted experiments in present study.

1.3 Organization of Report

This report includes four chapters. After this introduction, Chapter 2 presents the materials and testing procedures used in this study. Chapter 3 presents and discuss the experimental results. Finally, Chapter 4 summarizes the main findings and conclusions of this study.

Chapter 2. Materials and Methods

2.1 Materials

Since PG 64-XX asphalt binders are the most common binders used in central part of the United States, two chemically different PG 64-XX binders, purchased from different companies (denoted by F64 and J64), were selected for phase 1 of this study. For verification purposes (phase 2), one unmodified binder PG 58-XX (denoted by T58), three highly modified asphalt binders including PG 70-XX binder (denoted by J70), PG 76-XX (denoted by J76), and PG 82-XX (denoted by F82), were chosen. It should be noted that the first letter in naming of binders (i.e., F, J, and T) refers to the source of the binder. The properties of binders are presented in Table 1.

Table 1. Properties of asphalt binders used in the study.

Test	Standard	Asphalt Binder					
		F64	J64	T58	J70	J76	F82
Specific gravity (25 °C)	ASTM-D70 [24]	1.031	1.024	1.027	1.034	1.033	1.028
Viscosity (135 °C) cSt	ASTM-D4402 [25]	759	1700	280	311	652	2712
PG (-)	ASTM-D7643 [26]	64-XX	64-XX	58-XX	70-XX	76-XX	82-XX
SARA Fractions	IP-469 [27]						
Asphaltene		18.6	16.8	14.7	16.6	19.0	19.4
Resin		25.9	23.5	23.4	25.8	25.7	28.1
Aromatic		50.3	53.9	56.6	52.9	50.5	47.9
Saturate		5.3	5.8	5.3	4.7	4.9	4.6
Elemental Analysis							
Carbon		82.91	83.67	83.59	83.37	83.81	83.87
Hydrogen		10.80	10.62	11.33	10.79	10.92	10.80
Nitrogen		0.52	<0.50	0.64	0.58	0.57	0.58
Oxygen		1.58	<0.50	<0.5	<0.50	<0.50	<0.50
Sulfur		4.61	4.82	4.03	4.64	5.19	4.19

2.2 Methods

2.2.1 Rolling Thin Film Oven (RTFO) and Pressure Aging Vessel (PAV)

To duplicate the effects of short-term aging of asphalt binder, the typical process of using a RTFO following the ASTM-D2872 [9] test method was employed, and applied to all samples. To study the effect of pertinent parameters and their probable interactions, different combinations of three levels of temperatures, times, airflows, and weights of asphalt binder were considered as listed in Table 2.

The PAV test [28] is performed to simulate the long-term aging of asphalt binder. In the PAV procedure, 50 gr of the RTFO aged binder is used. The temperature of the aging is maintained at 100 ºC for 20 hours at a pressure of 2.1 MPa. More details about the long-term aging process is described in ASTM D6521 [28].

2.2.2 High-End Performance Grade (PG)

In order to determine the complex shear modulus (G^*) and phase angle (δ) of aged binders, a dynamic shear rheometer equipped with standard 25mm diameter plates at a 1mm testing gap was used. The temperature at which the permanent deformation (rutting) parameter($G^*/\sin\delta$) of short-term (RTFO) aged binders meet the performance grade (PG) criterion [29] was recorded as the continuous high-end PG of each binder.

2.2.3 Low-End Performance Grade (PG)

To determine the temperatures at which relaxation constant (m) and flexural creep stiffness (S) at 60 s of loading were equal to 0.300 and 300 kPa, respectively [30], Bending Beam Rheometer (BBR) tests were performed on binder samples aged through RTFO plus PAV procedures. Then, the obtained temperatures were used to determine the continuous low-end PG of each binder [26, 31].

2.2.4 Kinematic Viscosity (KV)

Typically, there are three “viscosity” tests that can be run on binder: 1) Rotational Viscosity, 2) Vacuum Capillary, and 3) Kinematic Viscosity. Due to sample availability, kinematic viscosity was used to characterize the flow behavior of the binder. The typical temperatures used in the kinematic viscosity test procedure are 60 °C and 135 °C. A glass capillary kinematic viscometer tube with calibrated timing marks is charged with binder and then conditioned to the closely regulated temperature of either 60 °C or 135 °C. The binder is then gravity-induced to pass through the tube capillary and timed as it passes through the marks. The kinematic viscosity value is determined by multiplying the efflux time in seconds between the timing marks, by the tube's viscometer calibration factor [32]. In this study a Koehler KV3000 was used to perform viscosity test at 135 °C.

2.2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

A Nicolet Avatar 380 FT-IR spectrometer operated in attenuated total reflection (ATR) mode was chosen for performing FT-IR test. The spectra were recorded within 400 to 4,000 cm^{-1} wavenumber range with a resolution of 4 cm^{-1}. OMNIC 8.1 software was applied to estimate the areas under the peaks. The aging of asphalt binders is typically monitored by the carbonyl and sulfoxide indices; however, the sulfoxide index is limited in identification of the level of binder oxidation due to aging [33-36]. This may be partially due to the similar concentrations of sulfur in the binders, the low level of sulfur relative to carbon, and thermal instability of sulfoxide containing species [37]. Therefore, only the carbonyl index (IC=O)was considered as the criterion of asphalt binder aging as [38, 39]:

$$\text{Carbonyl Index (IC=O)} = (\text{Area under Band } 1700 cm^{-1})/(\Sigma \text{ Area under FT} - \text{IR Spectrum}) \qquad \textbf{Eq. 1}$$

2.2.6 Saturate-Aromatic-Resin-Asphaltene (SARA) Analysis

In order to estimate the percentage of the asphalt binder component (i.e., SARA) in different asphalt binders, an Iatroscan MK-6 was employed. The Iatroscan method is based on solubility and polarity. Firstly, the asphaltenes are separated from the bulk asphalt as the materials are insoluble in n-heptane. This is a separate test procedure and is not performed by the Iatroscan equipment. Once the n-heptane insoluble material is removed from the asphalt the remaining material (generally referred to as maltenes) are further separated based on their relative solubility in different solvents using an Iatroscan MK-6.

2.2.7 Elemental Analysis

The oxygen determination using a Thermo Finnigan FlashEA™ Elemental Analyzer was made to detect the oxygen content of asphalt binders. During the pyrolysis, nitrogen, hydrogen, and carbon monoxide are formed when they contact the nickel-plated carbon catalyst at 1,060 °C. The pyrolysis products cross an adsorption filter where halogenated compounds are retained. The carbon monoxide, hydrogen, and nitrogen are separated via a chromatographic column. The FlashEA 1112 then automatically analyzes the carbon monoxide in a self-integrating, steady state thermal conductivity analyzer, and provides the oxygen percentage. In order to determine sulfur in binders, the sulfur dioxide as the product of sample combustion reaction (1350 + 50 °C in pure oxygen atmosphere), was analyzed using infrared absorption technique (SC-632 sulfur determinator). To determine the amount of carbon, hydrogen, and nitrogen, samples were burned in a pure oxygen atmosphere at 920 – 980 °C and the resulted combustion products (CO_2, H_2O, and N_2) were analyzed by using the PerkinElmer 2400 Series II CHNSO Analyzer.

2.3 Design of Experiments: Response Surface Methodology (RSM)

Response surface methodology (RSM) is a statistical approach that has been employed in various fields of science engineering [22, 40-49] with different purposes. This study seeks to employ an RSM concept as follows:

1. To establish an observable relationship, at least an approximate one, garnered between the response and the parameters that can be used to predict the response value for a various given setting of the control parameters applied.
2. To use the practice of testing hypothesis to determine the significance of the parameters being applied.
3. To determine an estimate for the optimum settings of those parameters that results in the desired response over a certain chosen region of interest.

In order to develop a second order polynomial model, a central composite design (CCD) using multiple linear regression was used to estimate the model coefficients, by setting each factor at its high level (+1), low level (-1), and medium level (0). A quadratic polynomial regression model (Eq. 2) was applied in order to estimate and predict the response value over a range of input factors' values [50]:

$$Y = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} b_{ij} X_i X_j \quad \textbf{Eq. 2}$$

where Y is the dependant response variable (i.e., IC=O and high-end PG), b_0 is the intercept term, b_i, b_{ii}, and b_{ij} are the measures of the effect of variable X_i, X_j and X_iX_j, respectively. X_i and X_j represent the independent variables and k is the number of these factors. In this case k is four as it includes time, temperature, airflow and asphalt binder weight. The variable X_iX_j represents the first order interaction between X_i and X_j ($i < j$).

Chapter 3. Results and Discussion

Twenty-five combinations were generated by the principle of RSM. The primary variables influencing IC=O and high-end PG from the RTFO protocol are time, temperature, airflow rate, and the weight of binder. The factors will be investigated using a variable set at 3 levels, for example for temperature: high level (e.g., temperature = 183 °C), low level (e.g., temperature = 143 °C) and medium level (e.g., temperature = 163 °C). The specific level for each of the operational parameters, according to a CCD, are listed in Table 2. All of the specimens are tested using three replicates, and the final result is reported as a mean value. This is performed in a randomized order to avoid systematic bias. Finally, the data model is analysed using MINITAB Release 17 to predict the main effective factors.

Table 2. Central composite design arrangement and responses for asphalt binders.

Run	Aging Parameters				Responses			
					High-End Performance Grade (°C)		IC=O	
	Time (min)	Temperature (C)	Airflow (l/min)	Weight (gr)	F64	J64	F64	J64
1	45	143	3	15	61.3	62.0	0.000417	0.003812
2	125	143	3	15	68.1	68.6	0.001237	0.007402
3	45	183	3	15	70.3	70.6	0.000971	0.006362
4	125	183	3	15	85.5	85.7	0.002946	0.014549
5	45	143	5	15	62.3	62.1	0.000367	0.001176
6	125	143	5	15	67.9	67.7	0.000914	0.004047
7	45	183	5	15	70.4	71.3	0.000965	0.006716
8	125	183	5	15	86.0	86.9	0.002666	0.015213
9	45	143	3	35	60.6	61.0	0.000254	0.002761
10	125	143	3	35	64.0	65.1	0.000713	0.003731
11	45	183	3	35	64.5	64.8	0.000594	0.003164
12	125	183	3	35	73.6	73.7	0.001082	0.009140
13	45	143	5	35	60.9	61.3	0.000199	0.002353
14	125	143	5	35	64.0	65.1	0.000742	0.004297
15	45	183	5	35	64.5	65.5	0.000441	0.003894
16	125	183	5	35	74.0	74.8	0.001623	0.009161
17	45	163	4	25	63.5	64.1	0.000525	0.004412
18	125	163	4	25	71.3	72.1	0.001219	0.007947
19	85	143	4	25	62.9	63.4	0.000347	0.004575
20	85	183	4	25	72.7	73.5	0.001305	0.008481
21	85	163	3	25	67.5	68.0	0.000867	0.007086
22	85	163	5	25	67.3	67.2	0.000930	0.004782
23	85	163	4	15	71.5	71.4	0.000967	0.007849
24	85	163	4	35	66.0	66.2	0.000650	0.004199
25	85	163	4	25	67.7	68.1	0.000840	0.004488

3.1 Model Fitting

The ANOVA tables for high-end PG and IC=O of F64 and J64 are presented in Table 3 and Table 4. The P-value of models is less than 0.1 (Table 3 and Table 4) and the fact that the error contribution for the models is less than 5%, which is considered as an insignificance error, indicate the suitability of the models. According to the results shown in Table 3 and Table 4, the first order terms of time, temperature, and weight significantly affect the high-end PG and IC=O of F64 of J64; in addition, the interactive terms of time–temperature, time–weight and temperature–weight are statistically significant within the studied range. On the other hand, only the quadratic term of weight is significant in the case of high-end PG of F64 and J64 asphalt binders.

Based on the calculated regression coefficients calculated by MINITAB software, the polynomial regression model equations are proposed as follows:

High-End $_{F64}$ = 26.43 - 0.2143 Time (min) + 0.2453 Temperature (°C) + 0.723 Weight (gr) + 0.01068 Weight (gr) × Weight (gr) + 0.002397 Time (min) × Temperature (°C) - 0.002822 Time (min) × Weight (gr) - 0.007987 Temperature (°C) × Weight (gr) **Eq. 3**

High-End $_{J64}$ = 21.50 - 0.1957 Time (min) + 0.2777 Temperature (°C) + 0.849 Weight (gr) + 0.01043 Weight (gr) × Weight (gr) + 0.002256 Time (min) × Temperature (°C) - 0.002603 × Time (min) × Weight (gr) - 0.008712 Temperature (°C) × Weight (gr) **Eq. 4**

IC=O$_{F64}$ = -0.00378 - 0.000017 Time (min) + 0.000023 Temperature (°C) + 0.000145 Weight (gr) + 0.0000001 Time (min) × Temperature (°C) - 0.0000001 Time (min) × Weight (gr) - 0.000001 Temperature (°C) × Weight (gr) **Eq. 5**

IC=O$_{J64}$ = -0.01558 - 0.000144 Time (min) + 0.000106 Temperature (°C) + 0.000706 Weight (gr) + 0.000001 Time (min) × Temperature (°C) - 0.000001 Time (min) × Weight (gr) - 0.000004 Temperature (°C) × Weight (gr) **Eq. 6**

The R^2 of Eq. 3 to Eq. 6 is 99.49, 98.96, 91.64, and 91.87% respectively.

Table 3. ANOVA table for high-end PG and IC=O for F64 asphalt binder.

Source	DF	Contribution (%)	F-Value	P-Value	Significant	Sign in Regression Model
			High-End PG			
Model	14	99.69	229.44	0.000	Yes	
Linear	4	87.62	705.80	0.000	Yes	
Time	1	30.86	994.50	0.000	Yes	Negative
Temperature	1	42.81	1379.33	0.000	Yes	Positive
Airflow	1	0.02	0.58	0.465	No	Not Assigned
Weight	1	13.93	448.81	0.000	Yes	Positive
Square	4	0.58	4.64	0.022	Yes	
Time×Time	1	0.14	0.24	0.637	No	Not Assigned
Temperature×Temperature	1	0.11	0.44	0.523	No	Not Assigned
Airflow×Airflow	1	0.00	0.32	0.587	No	Not Assigned
Weight ×Weight	1	0.32	10.41	0.009	Yes	Positive
2-Way Interaction	6	11.50	61.74	0.000	Yes	
Time ×Temperature	1	5.63	181.49	0.000	Yes	Positive
Time ×Airflow	1	0.00	0.08	0.778	No	Not Assigned
Time ×Weight	1	1.95	62.78	0.000	Yes	Negative
Temperature ×Airflow	1	0.00	0.00	1.000	No	Not Assigned
Temperature ×Weight	1	3.91	125.98	0.000	Yes	Negative
Airflow×Weight	1	0.00	0.08	0.778	No	Not Assigned
Error	10	0.31				
Total	24	100.00				
			IC=O			
Model	14	96.02	17.25	0.000	Yes	
Linear	4	80.52	50.63	0.000	Yes	
Time	1	37.44	94.17	0.000	Yes	Negative
Temperature	1	29.01	72.97	0.000	Yes	Positive
Airflow	1	0.03	0.07	0.794	No	Not Assigned
Weight	1	14.04	35.32	0.000	Yes	Positive
Square	4	1.46	0.92	0.490	No	
Time×Time	1	1.07	0.31	0.592	No	Not Assigned
Temperature×Temperature	1	0.13	0.04	0.851	No	Not Assigned
Airflow×Airflow	1	0.26	0.58	0.463	No	Not Assigned
Weight ×Weight	1	0.00	0.00	0.953	No	Not Assigned
2-Way Interaction	6	14.04	5.89	0.007	Yes	
Time ×Temperature	1	5.28	13.28	0.005	Yes	Positive
Time ×Airflow	1	0.03	0.08	0.782	No	Not Assigned
Time ×Weight	1	3.35	8.42	0.016	Yes	Negative
Temperature ×Airflow	1	0.15	0.38	0.553	No	Not Assigned
Temperature ×Weight	1	4.61	11.60	0.007	Yes	Negative
Airflow×Weight	1	0.62	1.56	0.240	No	Not Assigned
Error	10	3.98				
Total	24	100.00				

Abbreviation: DF, degrees of freedom.
Not Assigned: Since the term statistically is insignificant, it has been removed from polynomial regression model equations.

Table 4. ANOVA table for high-end PG and IC=O for J64 asphalt binder.

Source	DF	Contribution (%)	F-Value	P-Value	Significant	Sign in Regression Model
			High-End PG			
Model	14	99.49	140.44	0.000	Yes	
Linear	4	87.52	432.37	0.000	Yes	
Time	1	31.43	621.03	0.000	Yes	Negative
Temperature	1	43.45	858.70	0.000	Yes	Positive
Airflow	1	0.03	0.54	0.480	No	Not Assigned
Weight	1	12.61	249.19	0.000	Yes	Positive
Square	4	0.62	3.05	0.070	Yes	
Time×Time	1	0.29	0.14	0.712	No	Not Assigned
Temperature×Temperature	1	0.15	1.29	0.283	No	Not Assigned
Airflow×Airflow	1	0.00	0.63	0.447	No	Not Assigned
Weight ×Weight	1	0.17	3.41	0.094	Yes	Positive
2-Way Interaction	6	11.36	37.41	0.000	Yes	
Time ×Temperature	1	4.97	98.18	0.000	Yes	Positive
Time ×Airflow	1	0.00	0.02	0.888	No	Not Assigned
Time ×Weight	1	1.65	32.67	0.000	Yes	Negative
Temperature ×Airflow	1	0.10	2.00	0.188	No	Not Assigned
Temperature ×Weight	1	4.63	91.50	0.000	Yes	Negative
Airflow×Weight	1	0.00	0.07	0.794	No	Not Assigned
Error	10	0.51				
Total	24	100.00				
			IC=O			
Model	14	96.98	22.97	0.000	Yes	
Linear	4	80.85	67.02	0.000	Yes	
Time	1	32.78	108.68	0.000	Yes	Negative
Temperature	1	35.55	117.86	0.000	Yes	Positive
Airflow	1	0.80	2.64	0.135	No	Not Assigned
Weight	1	11.73	38.88	0.000	Yes	Positive
Square	4	0.24	0.20	0.934	No	
Time×Time	1	0.07	0.02	0.892	No	Not Assigned
Temperature×Temperature	1	0.13	0.55	0.475	No	Not Assigned
Airflow×Airflow	1	0.03	0.08	0.782	No	Not Assigned
Weight ×Weight	1	0.00	0.02	0.900	No	Not Assigned
2-Way Interaction	6	15.89	8.78	0.002	Yes	
Time ×Temperature	1	7.61	25.24	0.001	Yes	Positive
Time ×Airflow	1	0.00	0.00	0.970	No	Not Assigned
Time ×Weight	1	1.79	5.92	0.035	Yes	Negative
Temperature ×Airflow	1	1.28	4.24	0.660	No	Not Assigned
Temperature ×Weight	1	4.45	14.75	0.003	Yes	Negative
Airflow×Weight	1	0.77	2.54	0.142	No	Not Assigned
Error	10	3.02				
Total	24	100.00				

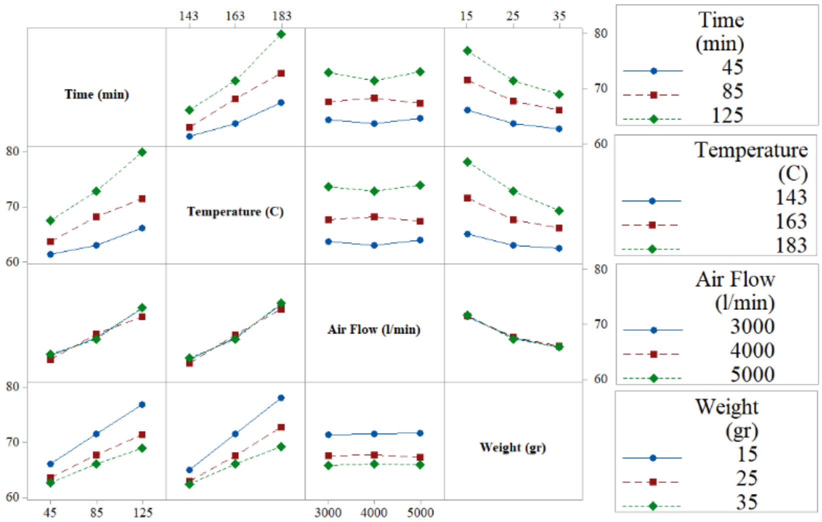
Abbreviation: DF, degrees of freedom.
Not Assigned: Since the term statistically is insignificant, it has been removed from polynomial regression model equations.

In Eq. 3 to 6, a chemical property (IC=O) as well as rheological characteristic (high-end PG) of the asphalt binders have been statistically correlated with two physicochemical parameters (time and temperature) and not only these two parameters directly affect the responses but also their interaction is significant. In addition, according to Eq. 3 to 6, an increase in the weight of asphalt binder poured in the RTFO bottle results in a decrease both in high-end PG and IC=O when time or temperature is kept constant. In the conventional RTFO protocol 35 gr binder can form a film thickness of 1.25 mm inside the bottle and a decrease in the weight of binder from 35 gr to 25 and 15 gr results in a reduction of film thickness by around 0.89 and 0.54 mm, respectively. This decrease in film thickness leads to a facile diffusivity of oxygen through the binder and intensifies the aging effects [51]. It should be pointed out that the airflow rate has no statistically significant effect on high-end and IC=O within the studied range of parameters which might be due to the fixed speed of RTFO carriage (15 $\pm$ 0.2 r/min). The results of this analysis indicate that the carriage speed, as the other influential parameters, should be tuned in accordance with the airflow rate as to whether such an interrelationship between the carriage speed and airflow rate in a RTFO process exists or not.

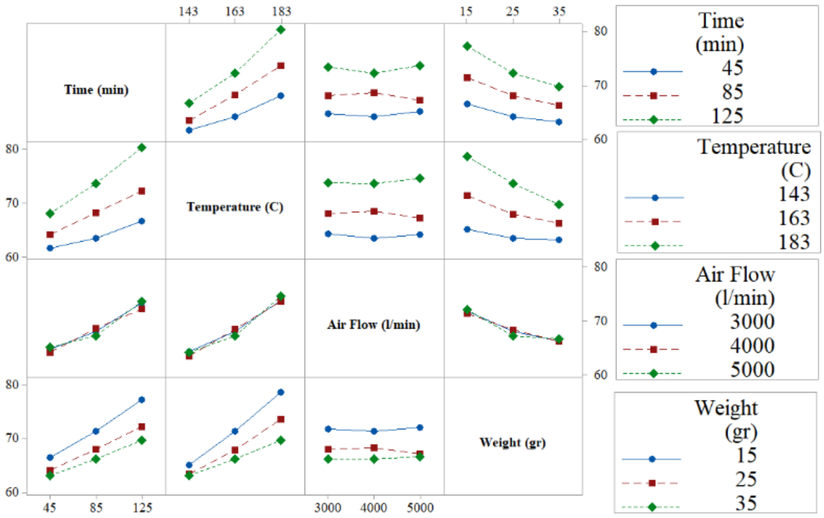
3.2 Interaction Effects

The interaction plots demonstrate how the relationship between one factor (e.g., time) and a response (e.g., high-end PG) depends on the value of the second factor (e.g., temperature). To interpret the interaction lines as shown in Figure 2, two types of lines need to be defined: (1) Parallel lines and (2) Nonparallel lines. In interaction plots, a parallel line means the interaction does not affect the relationship between the factors and the response, while a nonparallel line indicates an interaction occurs quite strongly, thus the more nonparallel and sloped the lines are, the greater the strength of the interaction. Although this plot displays the effects, the appropriate ANOVA test should be carried out to confirm the statistical significance of the effects.

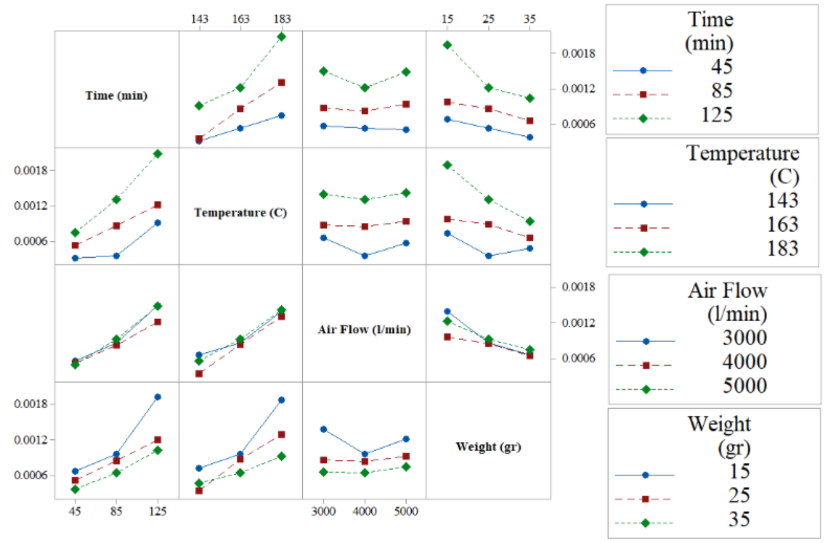
Figure 2(a) shows the interaction effect of factors on high-end PG of F64 binder. The results indicate that the interaction effect of airflow and other factors (i.e., time, temperature, and weight) does not affect high-end PG of F64 (parallel lines), while the interactions effect of other parameters are noticeable. Same trend is observed about the effect of airflow on High-End PG of J64. Although in some cases the interaction effect of airflow on carbonyl index (IC=O) of both binders (F64 and J64) produces a nonparallel line, the ANOVA test results presented in Table 3 and Table 4 confirm this effect is statistically insignificant.



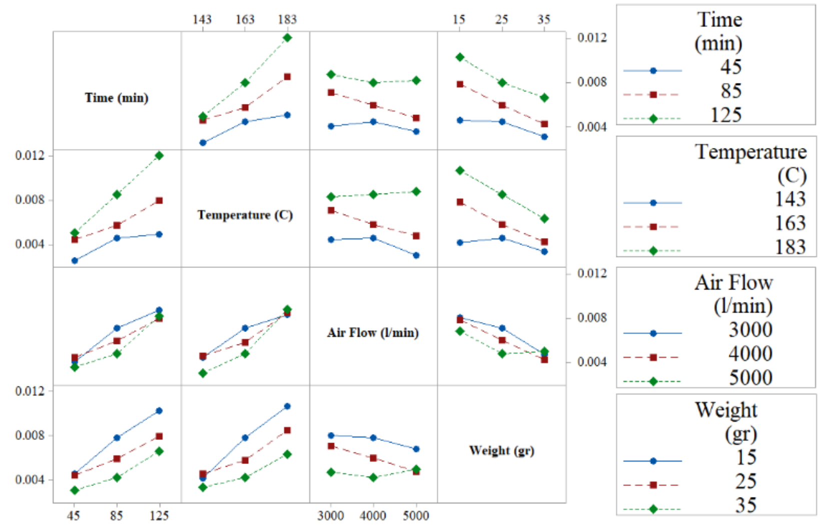
(a) High-End PG of F64



(b) High-End PG of J64



(c) IC=O of F64

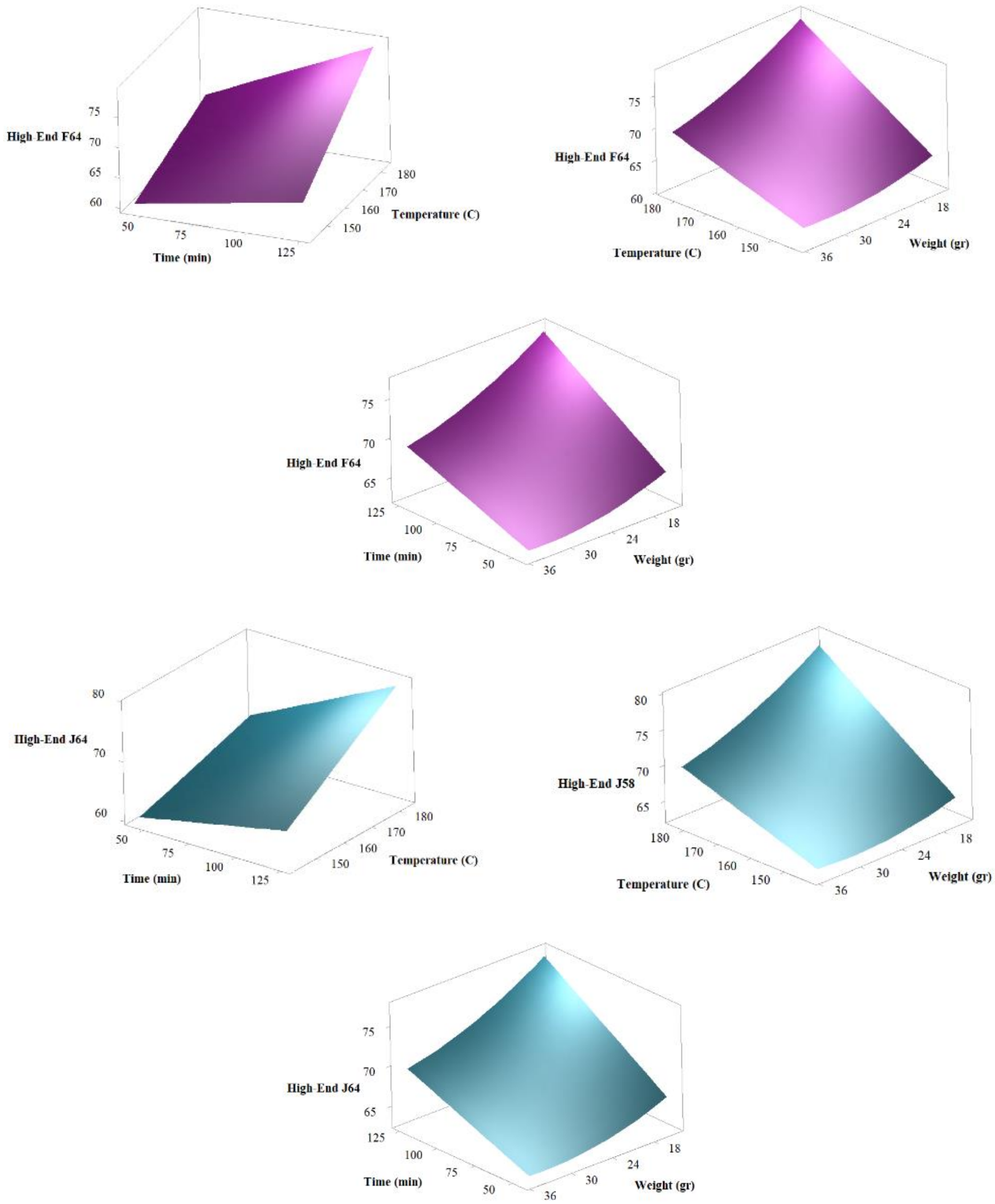


(d) IC=O of J64

Figure 2. Interaction plots of high-end PG and IC=O.

3.3 Effects of Parameters: Analysis of Response Surface

In the cases where interaction between factors is statistically significant, a 3-dimensional surface plot gives more complete information regarding the effect of a factor on the response [50]. The curvature of the 3-D surface plot presented in Figure 3 suggests that time, temperature, and weight of binder have interaction with each other for high-end temperature and carbonyl index. This is further confirmed by the results presented in Table 2. For instance, the surface plot of high-end F64 shows that at a constant Temperature (e.g., 183 °C) a decrease in weight results in increasing of the high-end temperature from around 68 to 78 °C. On the other hand, when the temperature is set at the lower value (143 °C), the increase in high-end temperature due to decrease of weight is lower. The same analysis can be performed on other responses (i.e., high-end J64, IC=O J64, and IC=O F64) and their surface plots.



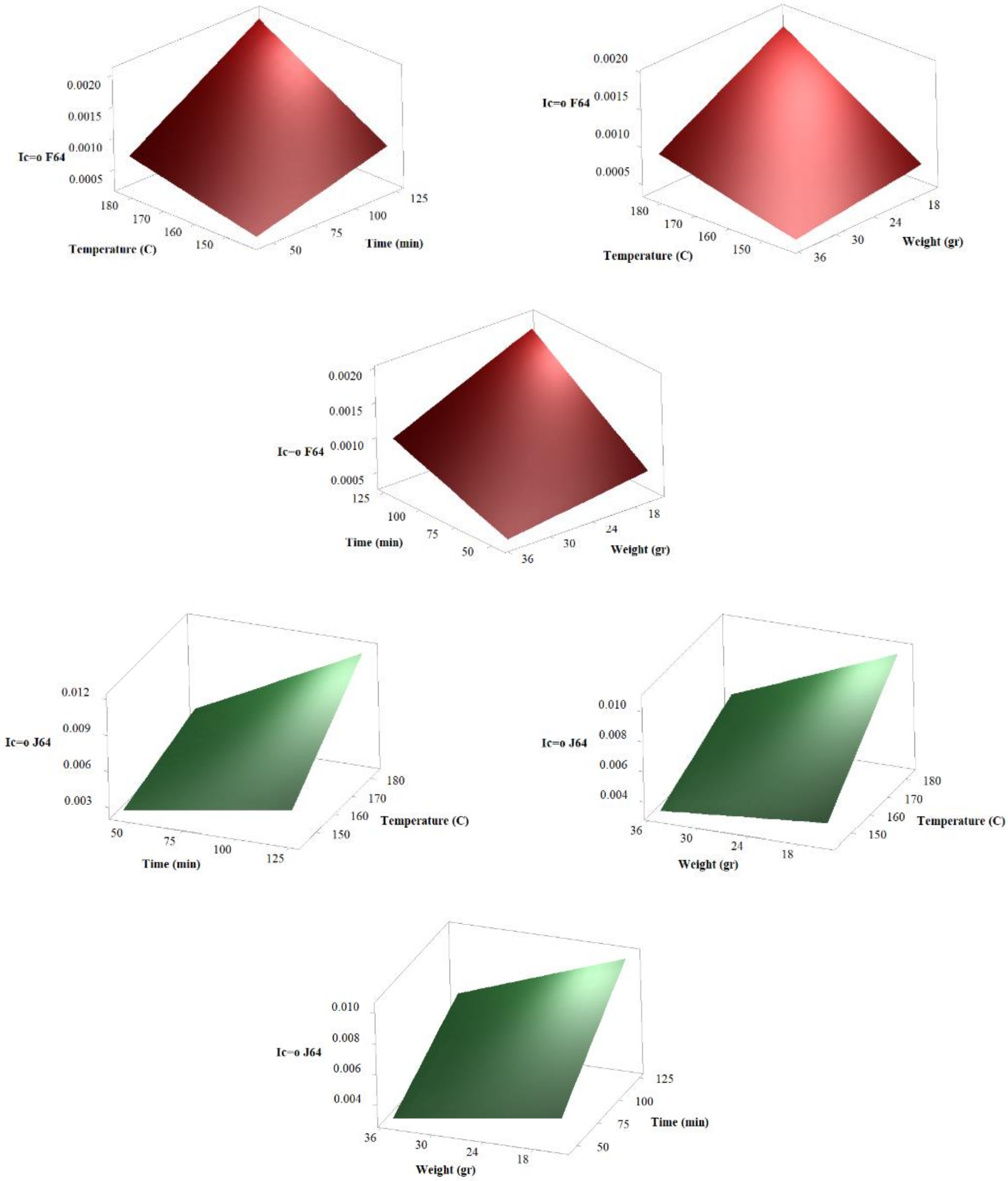
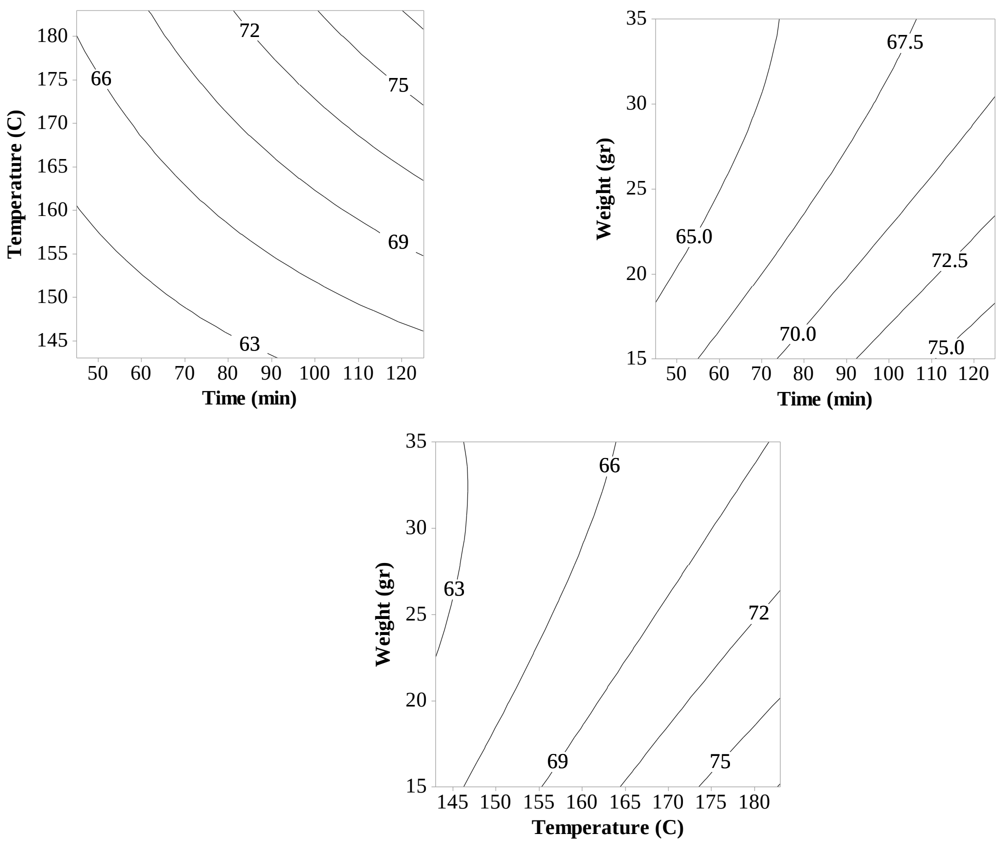
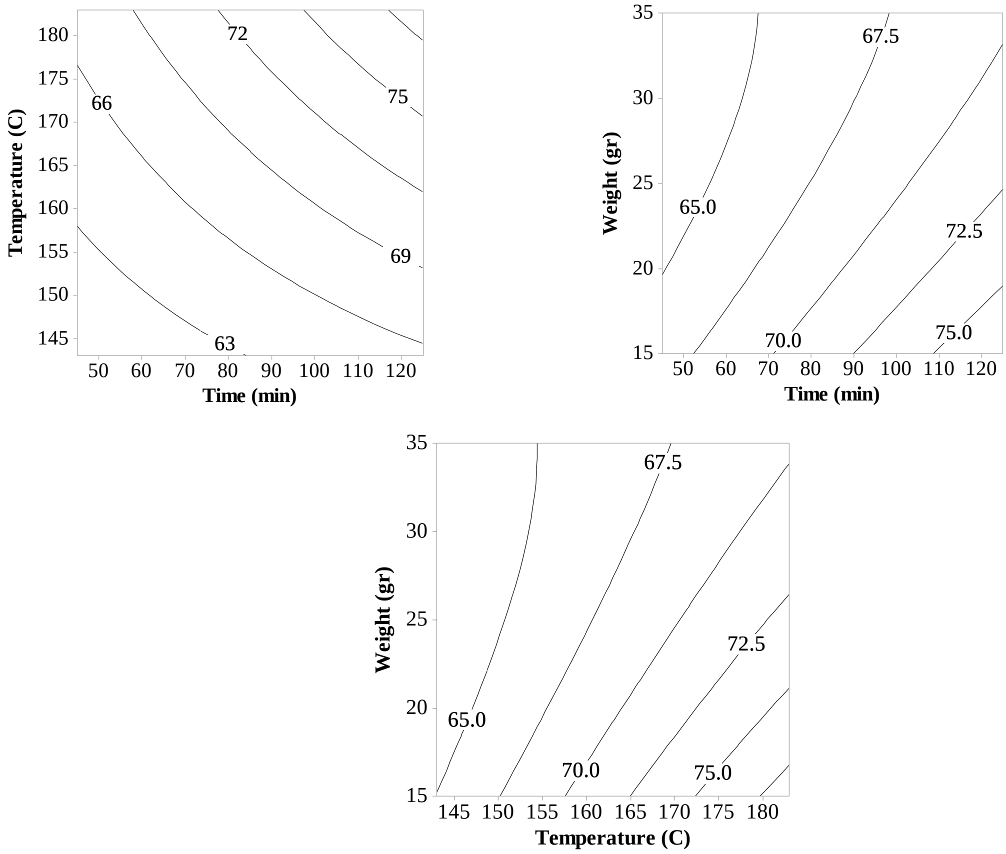


Figure 3. Surface plots.

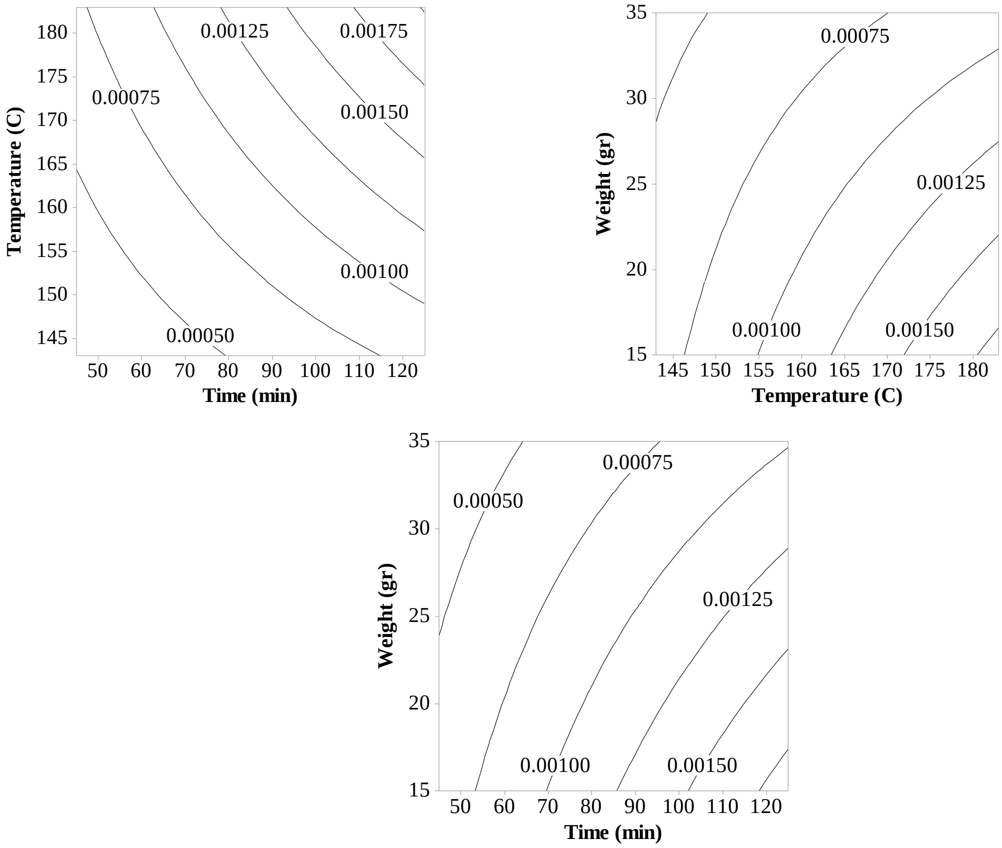
Generally, the relative effect of the parameters can be examined using contour plots, especially when the parameters did not have the same effect on the responses. Figure 4 illustrates the contour plots of high-end PG and IC=O for the asphalt binders versus time, temperature, and weight. As mentioned in section 5.1, the interactive terms of airflow with time, temperature, and weight are statistically insignificant for both responses (high-end PG and IC=O), and therefor their contour plots are not shown. The combination of aging factors (within the studied range) that result in an aged binder with the desired grade was selected. It is worthy of note that the desired grade is 66.01 °C and 66.24 °C (continuous high-end PG) for F64 and J64, respectively. For simplicity, it was assumed that the continuous high-end PG of both binders is 66 °C. In other words, any point on the curve of 66 °C in Figure 4(a) and (b) results in a high-end PG similar to that obtained under current RTFO protocol (time=85 min, pressure=2.1 MPa, temperature=163 °C, and weight of binder=35 gr). The same procedure can be conducted in the case of IC=O and the range where IC=O of binder is similar to that of aged under current RTFO protocol is obtained.



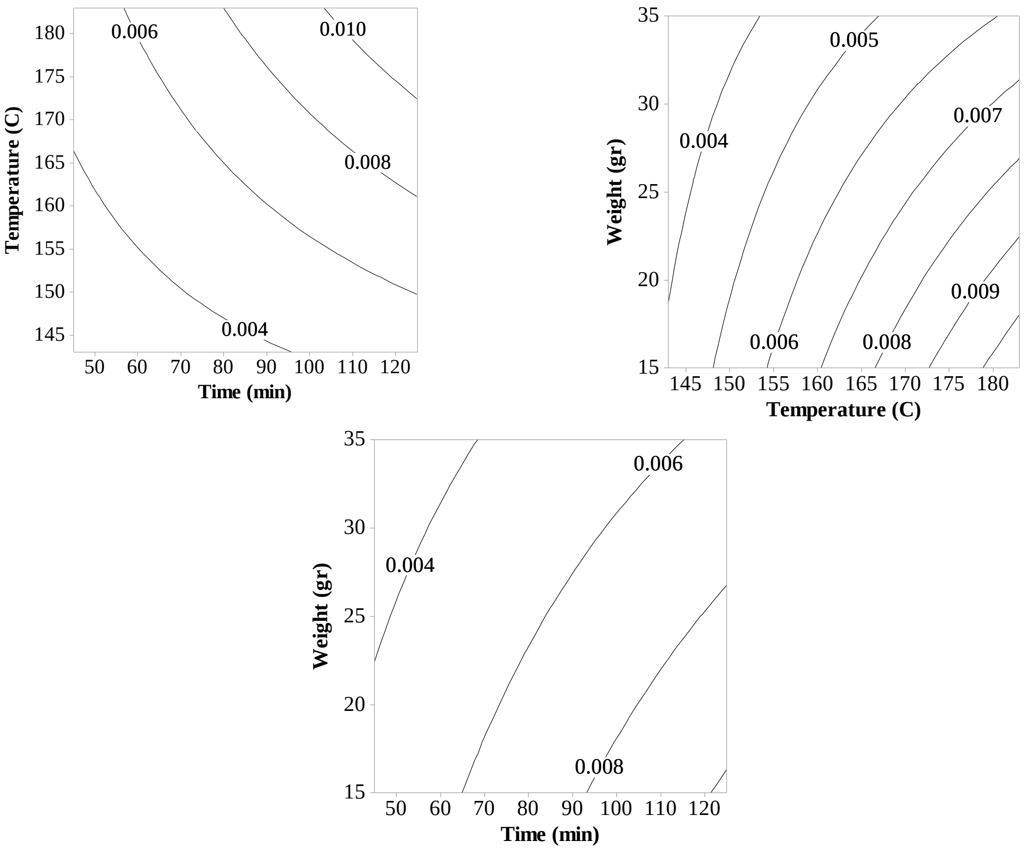
(a) High-End PG of F64



(b) High-End PG of J64



(c) IC=O of F64



(d) IC=O of J64

Figure 4. Contour plots of high-end PG and IC=O.

The combinations of parameters that results in high-end PG similar to that of obtained under conventional RTFO protocol are summarized in Table 5. It is worthy of note that the carboxylic anhydrides and small amounts of other highly oxidized species can be formed under severe aging conditions, and consequently, the binder hardening approaches its extreme [52]. Since such type of aging does not occur in the field aging process, these extreme conditions should be prevented, especially at elevated temperatures. The combinations of parameters which results in a carbonyl index similar to that obtained under conventional RTFO protocol are also estimated using contour plots as shown in Figure 4 (c) and (d) and summarized in Table 5. These combinations of parameters can be introduced as the alternative conditions for conducting RTFO aging. It should be pointed out that more studies on various binders with different grades and sources must be carried out towards arriving at a definite and comprehensive conclusion. However, as a beginning study, the following conditions are applicable for the simulation of two different binders (see viscosity, oxygen and asphaltene content of F64 and J64 shown in Table 1) with the same high-end PG, in a short-term aging process:

Time (min) = 45 min, Temperature = 180 °C, Weight = 25 gr, 3 l/min <Airflow< 5 l/min

The main advantages of these alternative conditions are the lower time needed for short-term aging and the lower amount of binder poured in the RTFO bottle that can avoid a spilling issue when RTFO carriage rotates. In addition, by increasing temperature to 180 °C, it is most likely that the fluidity becomes high enough inside the RTFO bottles, especially in the case of highly modified binders.

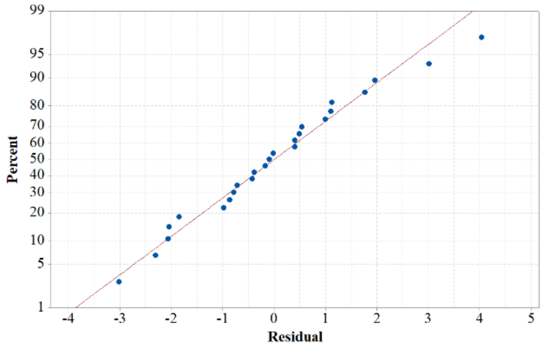
Table 5. Alternative RTFO aging parameters.

Alternative	Time (min)	Temperature (°C)	Weight (gr)
(a) Based on High-End PG of F64			
1	45	180	25
2	125	145	25
3	87	163	35
4	45	163	15
5	85	163	35
6	85	146	15
(b) Based on High-End PG of J64			
1	45	178	25
2	125	145	25
3	82	163	35
4	45	163	15
5	85	161	35
6	85	146	15
(c) Based on IC=O of F64			
1	47	176	25
2	100	145	25
3	80	163	35
4	48	163	16
5	85	161	35
6	85	143	16
(d) Based on IC=O of J64			
1	47	179	25
2	105	148	25
3	90	163	35
4	58	163	20
5	85	164	34
6	85	150	20

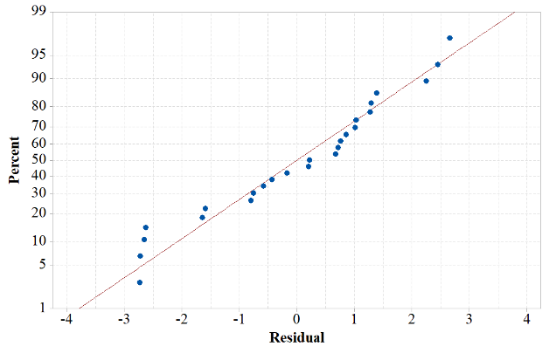
The authors realize that the recommended procedure yields less than 25 gr binder. It means that to have enough binder for one PAV pan and determine the low-end continuous PG based on BBR test results, three RTFO bottles should be used. It might be a concern for quality control production laboratories, as the current short-term aging protocol only needs two RTFO bottles to produce enough binder for one PAV pan. In other words, using current protocol, four different binders can be aged through RTFO at the same time; however, only two binders can be aged using the alternative/proposed protocol. This concern can be addressed by a new approach for determining low-end PG which uses 4-mm parallel plates on DSR as a replacement for BBR testing [53, 54]. The main advantages of this test method are: 1) it requires around 25 mg of RTFO+PAV aged binder instead of 12.5 gr to make one BBR beam, and 2) it does not need sample pre-molding. It should be noted that the BBR test is supposed to be performed with 2 beams, so in total 25 grams of binder is needed to run one BBR test. If 4 mm DSR process is accepted, one RTFO bottle will be sufficient for determining the low-end PG. However, another necessary modification would be reducing the PAV pan diameter to assure the same PAV aging in 20 hours.

3.4 Residual Analyses

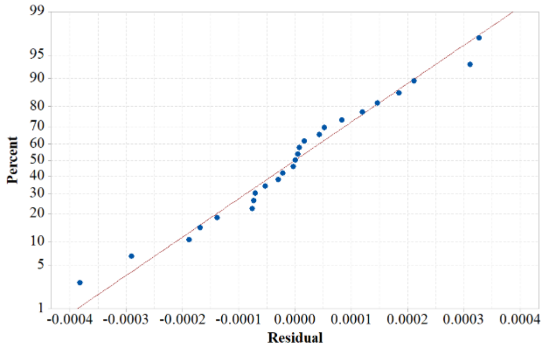
The verification of the suitability of the regression model for predictive purposes is carried out by residual analysis to confirm the normality of data [21]. Figure 5 and Figure 6 show the “Normal probability plot” and “Residual plot”. In the normal probability plot a straight, diagonal line indicates normally distributed data. Figure 5 shows the distribution of data follows a normal distribution pattern. On the other hand, the appropriate distribution of the data on both sides of the line in “residual plot” shows the suitability of the suggested model as shown in Figure 6.



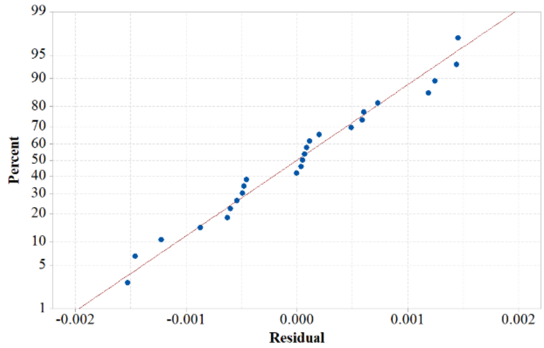
(a) High-End PG of F64



(b) High-End PG of J64

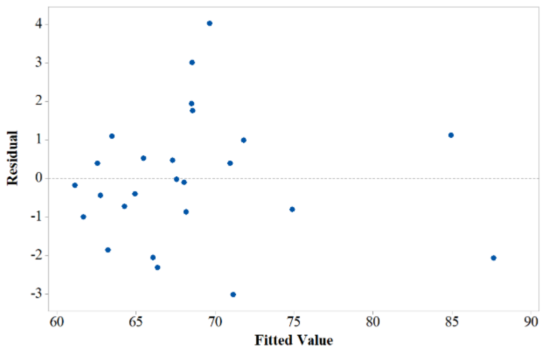


(c) IC=O of F64

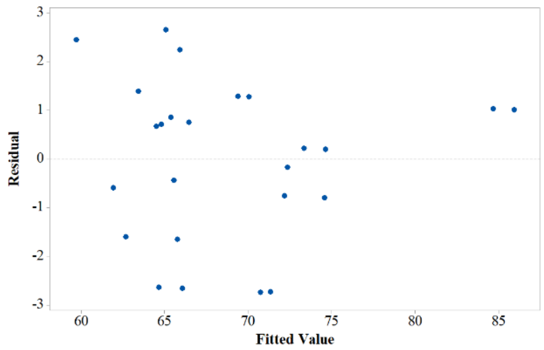


(d) IC=O of J64

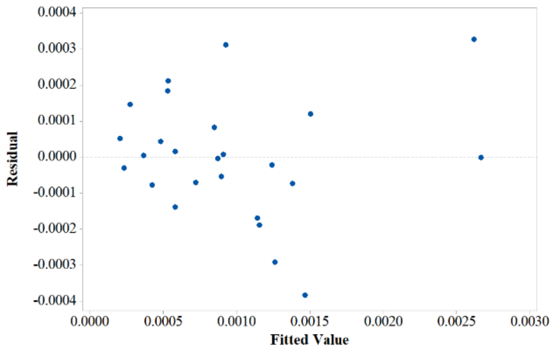
Figure 5. Normal probability plot.



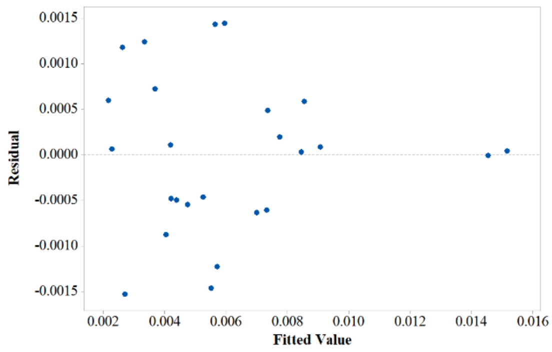
(a) High-End PG of F64



(b) High-End PG of J64



(c) IC=O of F64



(d) IC=O of J64

Figure 6. Residual plot.

3.5 Examination of the Proposed Protocol

In order to examine the applicability of the proposed short-term aging conditions, four asphalt binders including T58 (unmodified), J70 (modified), J76 (modified), and F82 (modified) were selected and aged under both current and proposed protocols. The rheological properties and chemical characteristics were characterized using different methods for comparison purposes. The average value of three replicates for high- and low-end PG, viscosity, and oxygen content as well as five replicates for IC=O, is shown in Table 6. According to the results presented in Table 6, there is a good agreement between the results of the proposed protocol and conventional protocol. In the case of high-end PG, the maximum absolute difference is around 0.22%, and a maximum absolute difference of 9.82% is observed in the case of kinematic viscosity. The crucial step for validation of the proposed protocol is to show that the higher aging temperature at shorter time does not alter the low-end PG compared to that of which is produced with the current RTFO procedure. The test results show that both short-term aging protocols result in the same low-end PG.

A comparison between the chemical properties of original (un-aged) binders (Table 1) and aged binder obtained under both protocols (Table 6), shows that the amount of oxygen content increases during the aging. This indicates that in RTFO aging, oxidation is a predominant process rather than loss of volatiles. In addition, the results reveal that the aging process leads to a change in SARA fractions of asphalt binders. As it can be seen in Table 6, during the aging process the conversion/oxidation of aromatics to resins, and resins to asphaltenes, occurs due to the presence of oxygen. However, saturates do not change significantly (compare SARA fraction of binders in Table 1 with their counterparts in Table 6).

It should be pointed out that no spillage was observed in the bottles when the aging temperature, time, and weight of binder were set at 180 °C, 45 min, and 25 gr respectively. However, the F82 binder had creeped out of the RTFO bottle when the current standard was employed.

Table 6. The rheological and chemical properties of T58 (unmodified), J70 (modified), J76 (modified), and F82 (modified) aged under current and alternative short-term aging protocol.

Properties	Aging Protocol	Binder			
		T58	J70	J76	F82
Continuous High-End PG (°C)	Current (NE/KS/IA) *	(61.3/60.6/61.7)	(74.7/74.0/74.0)	(80.8/80.3/80.1)	83.9
	Alternative (NE/KS/IA) *	(61.1/60.4/61.4)	(74.4/73.2/74.1)	(80.7/78.7/80.6)	83.7
Absolute Difference between Current and Alternative Protocol (%)		**(0.30/0.22/0.48)**	**(0.40/1.9/0.13)**	**(0.12/1.00/0.62)**	**0.23**
Continuous Low-End PG (°C)	Current (NE) *	-27.3	-24.6	-25.2	Not Assigned
	Alternative (NE) *	-27.0	-24.3	-24.1	Not Assigned
Absolute Difference between Current and Alternative Protocol (%)		**1.11**	**1.21**	**4.76**	**Not Assigned**
Kinematic Viscosity (cSt)	Current (NE/KS/IA) *	(433/425/401)	(1686/1602/1492)	(3329/3260/3217)	4030
	Alternative (NE/KS/IA) *	(436/421/407)	(1623/1506/1455)	(3209/2940/3071)	3753
Absolute Difference between Current and Alternative Protocol (%)		**(0.64/0.81/1.47)**	**(3.74/5.99/2.47)**	**(3.60/9.82/4.53)**	**6.87**
IC=O	Current	0.000448	0.000550	0.000647	0.000910
	Alternative	0.000432	0.000589	0.000618	0.000998
Absolute Difference between Current and Alternative Protocol (%)		**3.73**	**6.70**	**4.77**	**9.67**
SARA (Sa/Ar/Re/As) ** (%weight)	Current	5.1/52.1/25.3/17.5	4.6/49.6/25.8/20.0	4.4/47.7/26.9/21.0	5.1/47.7/24.4/22.8
	Alternative	5.2/52.5/24.9/17.3	5.5/48.6/25.9/20.6	4.6/48.7/25.6/21.1	5.0/46.8/25.8/22.5
Absolute Difference between Current and Alternative Protocol (%)		**0.44/1.92/0.76/1.61/1.16**	**8.00/2.06/0.39/2.91**	**4.35/2.05/5.08/0.47**	**2.00/1.92/5.43/1.33**
Elemental Analysis (C/H/N/O/S) *** (%weight)	Current	Not Assigned	83.63/11.30/0.61/0.82/4.53	83.69/11.22/0.60/0.78/4.49	83.57/11.07/0.57/0.80/4.50
	Alternative	Not Assigned	83.58/11.18/0.61/0.83/4.38	83.51/11.04/0.58/0.79/4.57	83.55/10.24/0.56/0.82/4.78
Absolute Difference between Current and Alternative Protocol (%)		**Not Assigned**	**0.06/1.06/0.00/1.22/3.31**	**0.22/1.60/3.33/1.28/1.78**	**0.02/7.5/1.75/2.50/6.22**

(NE/KS/IA) * = Nebraska DOT/Kansas DOT/Iowa DOT

(Sa/Ar/Re/As) ** = Saturate/Aromatic/Resin/Asphaltene

(C/H/N/O/S) *** = Carbon/Hydrogen/Nitrogen/Oxygen/Sulfur

Note: The average values of high-end PG, viscosity, and oxygen content (three replicates) as well IC=O (five replicates) are reported.

Note: Only the samples aged in Nebraska DOT are used for chemical analysis.

Chapter 4. Conclusion and Future Studies

4.1 Conclusion

In this study, a short-term laboratory-aging process with different combinations of aging duration, temperature, airflow, and weight of binder, according to central composite design, was conducted on two different binders for a better understanding of the effectiveness of aging parameters. The statistical analysis showed that the first order terms of time, temperature, and weight as well as their interactive terms were statistically significant. However, the effect of airflow rate, within the studied range, was insignificant. The results of the statistical analysis, for finding alternative conditions for the current laboratory short-term aging protocol, led to a new/alternative protocol in which the aging duration reduces to 45 min while the temperature increases to 180 °C. In addition, only 25 grams of binder and airflow rate between 3 l/min and 5 l/min were required for conducting the new short-term laboratory-aging process. For validation the new proposed protocol, one unmodified and three highly modified asphalt binders were employed, and the chemical and rheological properties of aged binders were compared to that of obtained under conventional laboratory aging protocol. The adequate consistency between the results of these two aging simulation protocols indicated the suitability and applicability of the new proposed protocol. This implied the other main advantage of the proposed protocol which was its applicability for both highly modified and unmodified asphalt binders.

4.2 Recommended Future Studies

This study does not address the laboratory short-term aging in warm mix asphalt (WMA) binder, a commonly used additive in today's asphalt mix production. A future mixture level study should be performed on both hot and warm mix asphalt using different binders and aggregate source and gradations to confirm the suitability of this alternative protocol for simulating/predicting the aging. The statistical methodology (RSM) and experimental design (CCD) used in this study vividly exhibit the robustness of these techniques which can significantly reduce the experimental efforts and is recommended to be used in the experimental studies and analyses.

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