

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

**Procedures for Using the California Model for
California Reformulated Gasoline Blendstocks
for Oxygenate Blending (CARBOB)**

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Note: The preexisting text is set forth below in normal type. The amendments are shown in *underline italics* to indicate additions and ~~strikeout~~ to indicate deletions.

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1. INTRODUCTION AND BACKGROUND

The procedures in this document describe how to use the ARB's model for California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB). The procedures are applicable when ethanol is being blended into California Reformulated Gasoline (RFG). The procedures can be used to comply with either the Phase 2 or Phase 3 gasoline regulations. For simplicity, the procedures described in this document will be referred to as the CARBOB procedures. CARBOB is the gasoline blendstock that, when blended with ethanol, results in a finished gasoline which meets the requirements of the Phase 2 or Phase 3 California Reformulated Gasoline (RFG) Regulations. The CARBOB procedures in this document are to be used in combination with the California Procedures for Evaluating Alternative Specifications for Phase 2 Reformulated Gasoline Using the California Predictive Model or with the California Procedures for Evaluating Alternative Specifications for Phase 3 Reformulated Gasoline Using the California Predictive Model (i.e., "The Predictive Model Procedures"). The Predictive Model Procedures implement Section 2265 of the California Code of Regulations, Gasoline Subject to PM Alternative Specifications Based on the California Predictive Model. The principal element of the Predictive Model Procedures is the Phase 2 or Phase 3 predictive model which is used to evaluate the emissions equivalency of alternative complying gasolines that producers wish to produce.

Under the predictive model provisions of the Phase 2 and Phase 3 RFG regulations, the refiner inputs into the predictive model equations the fuel properties of the gasoline he is interested in producing, referred to as the predictive model candidate gasoline. The predicted emissions associated with the candidate gasoline's properties are compared to the predicted emissions for a gasoline meeting either the Phase 2 or Phase 3 limits adopted by the Air Resources Board. If the predicted emissions for the refiner's predictive model candidate gasoline are equivalent to the predicted emissions for a gasoline meeting the appropriate reformulated gasoline limits (either Phase 2 or Phase 3), the predictive model candidate gasoline is allowed to be produced as an alternative complying gasoline.

Section 2266.5, Requirements Pertaining to California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB) and Downstream Blending contains the requirements governing the production and blending of CARBOB. These CARBOB procedures implement the use of the CARBOB model, which is the principle element of these procedures. The CARBOB model is a set of equations which predict the properties of the finished gasoline (gasoline after the addition of ethanol), given the properties of the CARBOB, the properties of the ethanol blended into the CARBOB, and the ethanol content of the finished gasoline. The CARBOB properties, the ethanol properties, and the ethanol content of the finished gasoline are inputs to the CARBOB model, and the properties of the finished gasoline are outputs. The finished gasoline outputs from the CARBOB model are then input into either the Phase 2 or Phase 3 predictive model (depending on which regulations are applicable), as the predictive model candidate gasoline, and the emissions equivalency of the predictive model candidate gasoline is evaluated in accordance with the Predictive Model Procedures.

Thus, the properties of the finished predictive model candidate gasoline can be determined without actually blending the ethanol into the CARBOB.

The purposes of CARBOB model are to facilitate the enforcement of the RFG regulations and to reduce the sampling and testing demands on the refiners in ensuring that gasolines containing ethanol meet the requirements of the RFG regulations. Enforcement is facilitated by allowing the enforcement staff to sample and test CARBOB and to compare the measured CARBOB properties to the properties reported to the ARB. The enforcement staff does not necessarily have to blend into the CARBOB ethanol in order to determine if the finished gasoline complies.

2. GENERAL USE OF THE CARBOB MODEL

As discussed above, the CARBOB model is a set of equations which relate the properties of finished gasoline (gasoline containing ethanol) to the properties of the CARBOB, the properties of the ethanol blended into the CARBOB, and the amount of ethanol that is blended. The CARBOB model uses these inputs to estimate the properties of the finished gasoline, which are then input into either the Phase 2 or Phase 3 Predictive Model. The Predictive Model then evaluates whether the finished gasoline meets the emissions equivalency requirements applicable to gasolines subject to the predictive model alternative specifications of the Phase 2 or Phase 3 gasoline regulations. Figure 1 illustrates schematically how the inputs and outputs to the CARBOB model are used in combination with the Predictive Model.

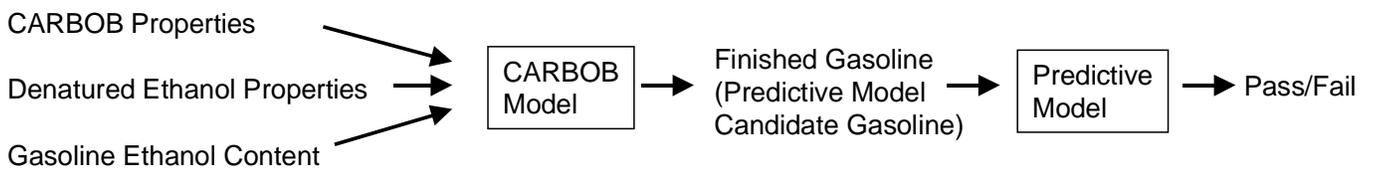
With the exception of the T50 distillation temperature and the oxygen content, the CARBOB model contains one equation for each fuel property regulated under the Phase 2 and Phase 3 RFG regulations. In the case of T50, there are two equations. There is one equation for T50 when the ethanol content of the gasoline is greater than or equal to 4.0 percent and less than 9.0 percent, and another equation when the ethanol content is from 9.0 to 10.0 percent (inclusive). If the ethanol content of the finished gasoline is less than 4.0 percent, the CARBOB model cannot be used. The CARBOB model does not contain an input for the oxygen content. The oxygen content of the predictive model candidate gasoline is input directly into either the Phase 2 or Phase 3 predictive model.

In using the CARBOB model, the user first indicates whether he intends to input into the CARBOB model proprietary values for the aromatics, olefins, sulfur, and benzene contents of the ethanol that is to be blended into the CARBOB. The presence of these compounds in the ethanol generally results from the use of a denaturant. If the user does not intend to use proprietary values for the aromatics, olefins, sulfur, and benzene contents, default values are used.

The user then enters into the CARBOB model the values of the CARBOB properties, and the amount of ethanol that is to be blended into the gasoline. The CARBOB model outputs the properties of the finished (ethanol-containing gasoline). The properties of the finished gasoline are input into either the Phase 2 or Phase 3

predictive model (whichever regulatory limits are appropriate) as the properties of the predictive model candidate gasoline. The emissions equivalency of the predictive model candidate gasoline is evaluated by the predictive model in accordance with the provisions of the Predictive Model Procedures.

Figure 1
Schematic Showing the Integration of the CARBOB Model with the Predictive Model



3. CARBOB MODEL EQUATIONS

The equations which constitute the CARBOB model are shown below:

A. RVP Model

$$RVP_{FG} = 1.446 + 0.961 * RVP_{CARBOB} \quad \text{where,}$$

RVP_{FG} is the RVP of the finished gasoline, in psi.

RVP_{CARBOB} is the RVP of the CARBOB, in psi.

B. T50 Models

There are two CARBOB models for T50. The first is for a finished gasoline ethanol content of greater than or equal to 4.0 percent, but less than 9.0 percent. The second is for a finished gasoline ethanol content of greater than or equal to 9.0 percent, but less than or equal to 10.0 percent.

i. Model for $4\% \leq \text{EtOH} < 9\%$

$$\begin{aligned} T50_{FG} = & 21.93 + 14.875 * \text{EtOH} - 10.238 * RVP_{CARBOB} + \\ & 0.672 * T50_{CARBOB} + 0.02579 * T90_{CARBOB} - 0.8313 * \text{EtOH}^2 - \\ & 0.3103 * RVP_{CARBOB} * \text{EtOH} + 0.06623 * T50_{CARBOB} * \text{EtOH} - \\ & 0.05519 * T90_{CARBOB} * \text{EtOH} + 0.03607 * RVP_{CARBOB} * T90_{CARBOB} \end{aligned}$$

where,

$T50_{FG}$ is the T50 of the finished gasoline, in degrees F,
 EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,

RVP_{CARBOB} is the RVP of the CARBOB, in psi,

$T50_{CARBOB}$ is the T50 of the CARBOB, in degrees F,

$T90_{CARBOB}$ is the T90 of the CARBOB, in degrees F.

ii. Model for $9\% \leq \text{EtOH} \leq 10\%$

$$\begin{aligned} T50_{FG} = & 559.276 - 0.5431 * RVP_{CARBOB} - 4.1884 * T50_{CARBOB} - \\ & 0.3957 * T90_{CARBOB} + 0.01482 * T50_{CARBOB}^2 - \\ & 0.05309 * T50_{CARBOB} * RVP_{CARBOB} + \\ & 0.02884 * T90_{CARBOB} * RVP_{CARBOB} \end{aligned}$$

where,

$T50_{FG}$ is the T50 of the finished gasoline, in degrees F,
 EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,

RVP_{CARBOB} is the RVP of the CARBOB, in psi,
T50_{CARBOB} is the T50 of the CARBOB, in degrees F,
T90_{CARBOB} is the T90 of the CARBOB, in degrees F.

Note that there is a T50 CARBOB model only for CARBOB ethanol contents greater than or equal to 4.0 percent. If the ethanol content of the CARBOB is less than 4.0 percent the CARBOB model can not be used.

C. T90 Model

$T90_{FG} = 1.493 + 0.964 * T90_{CARBOB} + 0.0468 * T50_{CARBOB} - 0.473 * EtOH$
where,

T90_{FG} is the T90 of the finished gasoline, in degrees F,
T90_{CARBOB} is the T90 of the CARBOB, in degrees F,
T50_{CARBOB} is the T50 of the CARBOB, in degrees F,
EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%.

D. Aromatic Content Model

$AROM_{FG} = ((1 - (EtOH * 0.01)) * AROM_{CARBOB}) + (EtOH * 0.01 * AROM_{EtOH})$
where,

AROM_{FG} is the aromatic content of the finished gasoline, in vol.%,
EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,
AROM_{CARBOB} is the aromatic content of the CARBOB, in vol.%,
AROM_{EtOH} is the aromatic content of the ethanol, in vol.%.

E. Olefin Content Model

$OLEF_{FG} = ((1 - (EtOH * 0.01)) * OLEF_{CARBOB}) + (EtOH * 0.01 * OLEF_{EtOH})$
where,

OLEF_{FG} is the olefin content of the finished gasoline, in vol.%,
EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,
OLEF_{CARBOB} is the olefin content of the CARBOB, in vol.%,
OLEF_{EtOH} is the olefin content of the ethanol, in vol.%.

F. Benzene Content Model

$$\text{BENZ}_{\text{FG}} = ((1 - (\text{EtOH} \cdot 0.01)) \cdot \text{BENZ}_{\text{CARBOB}}) + (\text{EtOH} \cdot 0.01 \cdot \text{BENZ}_{\text{EtOH}})$$

where,

BENZ_{FG} is the benzene content of the finished gasoline, in vol.%,
 EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,

$\text{BENZ}_{\text{CARBOB}}$ is the benzene content of the CARBOB, in vol.%,

$\text{BENZ}_{\text{EtOH}}$ is the benzene content of the ethanol, in vol.%.

G. Sulfur Model

$$\text{SULF}_{\text{FG}} = \{((1 - (\text{EtOH} \cdot 0.01)) \cdot \text{SULF}_{\text{CARBOB}} \cdot 0.718) + (\text{EtOH} \cdot 0.01 \cdot \text{SULF}_{\text{EtOH}} \cdot 0.788)\} / \{((1 - (\text{EtOH} \cdot 0.01)) \cdot 0.718) + (\text{EtOH} \cdot 0.01 \cdot 0.788)\}$$

where,

SULF_{FG} is the sulfur content of the finished gasoline, in ppm,
 EtOH is the ethanol content of the finished gasoline, including the denaturant, in vol.%,

$\text{SULF}_{\text{CARBOB}}$ is the sulfur content of the CARBOB, in ppm by wt.,

$\text{SULF}_{\text{EtOH}}$ is the sulfur content of the ethanol, in ppm by wt.

4. DETAILED APPLICATION OF THE CARBOB MODEL EQUATIONS

This section will provide a step-by-step explanation of the how the CARBOB model equations are used and how the outputs from the CARBOB model are input into the Predictive Model equations.

~~The first step in the process is for the user to decide if he is interested in using the evaporative emissions model element of the Phase 3 predictive model (if he is complying with the Phase 3 regulations). If the Phase 2 regulations are applicable, this step is not applicable because there is no evaporative emissions element associated with the Phase 2 predictive model. The user generally will not be interested in using the evaporative emissions model element of the Phase 3 predictive model if he is interested in complying with a flat 7.0 psi RVP limit instead of a limit less than 6.9 psi, or greater than 7.0 psi.~~

~~————~~The next step in the use of the CARBOB model is for the user to specify the properties of the ethanol that is to be blended into the CARBOB. The ethanol properties to be specified are: 1) the aromatic content (vol.%), 2) the olefin content (vol.%), 3) the sulfur content (wt. ppm), and 4) the benzene content (vol.%). If the user does not specify values for the ethanol properties, the CARBOB model uses default property values. The default property values are shown in Table 1 below. If the user specifies

values for the ethanol properties, they are to be specified to the same number of decimal places as is shown for the default properties.

Table 1
Default Ethanol Properties Values Used in the CARBOB Model

Property	Default Property
Aromatic content	1.7 vol.%
Olefin content	0.5 vol.%
Sulfur content	10 ppmw
Benzene content	0.06 vol.%

After the user specifies the ethanol properties (or elects to use the default ethanol property values), he specifies the values of the properties of the CARBOB and the ethanol content (including the denaturant) of the finished gasoline. The values of the CARBOB properties and ethanol content are specified to the number of decimal places shown in Table 2.

Table 2
Fuel Properties Specified in CARBOB Model

Fuel Property	Units	Decimal Places
Reid vapor pressure (RVP)	psi, max.	0.01
T50 Distillation Temperature (T50)	deg. F, max.	1.0
T90 Distillation Temperature (T90)	deg. F, max.	1.0
Aromatics Content	vol.%, max.	0.1
Olefin Content	vol.%, max.	0.1
Ethanol Content	vol.%, max.	0.1
Sulfur Content	ppmw, max.	1.0
Benzene Content	vol.%, max.	0.01

The user then uses the CARBOB model equations shown in Section 3 above and the values for each CARBOB property, ethanol property, and the ethanol content of the finished gasoline, to compute, for each property for which there is a CARBOB model, the corresponding property for the finished gasoline. The value for each property of the finished gasoline is then input into either the Phase 2 or Phase 3 predictive model as the predictive model candidate gasoline. The use of the Phase 2 or Phase 3 predictive model is dictated by which regulations are in effect or applicable to the user at the time. The applicable Predictive Model then evaluates the emissions equivalency of the predictive model candidate gasoline in accordance with the process described in the Phase 2 and Phase 3 Predictive Model Procedures.

If the user intends to produce gasoline in which at least one property will comply with the predictive model averaging compliance option, and the user is establishing a DAL for the CARBOB in accordance with section 2266.5(a)(5)(B), the CARBOB model

must be used to calculate the designated alternative limit (DAL) for the final blend of oxygenated gasoline.

For the gasoline aromatic content, olefin content, benzene content, and sulfur content, the DAL for the final blend of oxygenated gasoline is calculated directly from the CARBOB models for these properties by inputting into the CARBOB models for these properties the DAL for the CARBOB. The CARBOB model prediction is the DAL for the final blend of oxygenated gasoline.

The methodology described above is also used in calculating the T50 and T90 DALs for final blends of oxygenated gasoline, with one exception. This exception occurs if a producer is producing gasoline in which the T50 will comply with a predictive model flat limit and the T90 will comply with a predictive model averaging limit, or the T50 will comply with a predictive model averaging limit and the T90 will comply with a predictive -model flat limit. In these cases, the DAL for the final blend of oxygenated gasoline is calculated by inputting into the CARBOB model the value of the CARBOB DAL for the property (either T50 or T90) which is being produced to the predictive model averaging limit, and inputting into the CARBOB model the flat limit of the CARBOB property (T50 or T90) that is being produced to the predictive model flat limit. The CARBOB model prediction is the DAL for the final blend of oxygenated gasoline for the property being produced under the predictive model averaging compliance option.

A minimum RVP requirement for CARBOB would be in effect during the non-RVP control period (i.e., the time in which the RVP limits specified in Section 2262 are not in effect). The purpose of this “wintertime” RVP specification is different from the purpose of the summertime RVP requirement for CARBOB or final blend of oxygenated gasoline. The purpose of the non-RVP control period minimum RVP requirement is to ensure that the T50 of a final blend of oxygenated gasoline is not greater than the value predicted by the CARBOB model. The minimum RVP requirement for the non-RVP control period arises as a consequence of the RVP term in the T50 CARBOB model. The T50 CARBOB model predicts that the T50 of a final blend of oxygenated gasoline decreases as the RVP of the CARBOB increases. Thus, while there are no basic flat or average RVP limits for CARBOB or gasoline that is not subject to the maximum RVP standards in section 2262, it is still necessary to specify the RVP of the CARBOB during the non-RVP control period in order to make a prediction for the T50 of the final blend of oxygenated gasoline. The RVP value that is used in making this prediction becomes a minimum allowable RVP for the particular blend of CARBOB during the non-RVP control period. That is, during the non-RVP control period, the CARBOB produced by the refiner is required to have an RVP greater than or equal to the value used in the T50 CARBOB model. This ensures that the final blend of oxygenated gasoline has a T50 less than or equal to that predicted by the T50 CARBOB model.

Shown in Table 3 on the next page is a worksheet which includes a step-by-step process to illustrate the use of the CARBOB procedures and to assist the user in using the CARBOB model. The worksheet in Table 3 assumes that the user is complying with

the Phase 3 regulations, but the same process would be used if the user were complying with the Phase 2 regulations. Only Step 5 in the process shown in Table 3 would be different if the user were complying with the Phase 2 gasoline regulations. In that case, the user would compare his predictive model candidate gasoline to the applicable Phase 2 limits instead of the Phase 3 limits.

Table 3
Worksheet for Computing Finished Gasoline Properties from CARBOB Properties

Step 1: Do you elect to use the evaporative emissions model element of the Phase 3 Predictive Model? Yes (Y) or No (N)

Step 2: Specify the properties of the ethanol, or use the default values in the table below.

Property	Specified Value	Default Value
Aromatic content (vol.%)		1.7
Olefin content (vol.%)		0.5
Sulfur content (ppmw)		10
Benzene content (vol.%)		0.06

Step 3: Specify the ethanol content, including the denaturant, in volume percent, of the finished gasoline. Ethanol content = _____ vol. percent.

Step 4: Enter in the table below the values of the CARBOB properties. For these CARBOB property values, and the ethanol properties specified in Step 2, and the ethanol content specified in Step 3, use the CARBOB model equations shown in Section 3 to compute the properties of the finished gasoline. Enter both the CARBOB values and the predicted finished gasoline values in the table below.

Property	CARBOB Value	Predicted Finished Gasoline Value ¹
RVP (psi)		
T50 (deg. F)		
T90 (deg. F)		
Aromatics (vol.%)		
Oxygen as Ethanol (max.) (vol.%)	Not Specified by User	
Oxygen as Ethanol (min.) (vol.%)	Not Specified by User	
Sulfur (ppmw)		
Benzene (vol.%)		

1 – The maximum and minimum oxygen values are specified by the user and are not predicted by the CARBOB model.

Step 5: Complete Table 7 of the Phase 3 Predictive Model Procedures by entering into column 2 (Candidate Fuel Specifications) of Table 7 of the Phase 3 Predictive Model Procedures the predicted finished gasoline property values from Step 4. For convenience,

Table 7 of the Phase 3 Predictive Model Procedures is shown on the next page. Proceed with the evaluation of the candidate fuel in accordance with the requirements specified in the Phase 3 predictive model Procedures.

Table 4
(Table 7 of Predictive Model Procedures)
Optional Worksheet for Candidate and Reference Fuel Specifications

Does the applicant wish to use the evaporative HC emissions model and the CO adjustment factor in the evaluation of the equivalency of the candidate fuel specifications? YES ___ NO ___

If the above question is answered yes, the flat RVP limit is 6.90 psi and the RVP cap is 7.20 psi. If the above question is answered no, 7.00 psi is the flat RVP limit and the candidate fuel RVP specification.

Does the applicant wish to certify a fuel containing ethanol? YES _____ NO _____

If the above question is answered yes, then the flat RVP limit is 7.00 psi and the RVP cap is 7.20 psi. If the above question is answered no, then 6.90 psi is the flat RVP limit for the candidate fuel RVP specification.

Fuel Property	Candidate Fuel ¹ : Specifications	Compliance Option: Flat or Average	Reference Fuel: Phase 3 RFG Specifications	
			(Circle Option Chosen)	
			Flat	Average
RVP		Flat	6.90 ⁵ / 7.00	None
Sulfur			20	15
Benzene			0.80/1.00 ⁶	0.70
Aromatic			25.0/35.0 ⁶	22.0
Olefin			6.0	4.0
Oxygen ² (Total)	(min)	Flat-Range	(min)	None
	(max)		(max)	
Oxygen ³ (as MTBE)	(min)	Not Applicable	Not Applicable	None
	(max)			
Oxygen ⁴ (as EtOH)	(min)	Not Applicable	Not Applicable	None
	(max)			
T50			213/220 ⁶	203
T90			305/312 ⁶	295

note: Footnotes are on the next page

Footnotes for Table 4

- 1 The fuel property value must be within or equal to the cap limit.
- 2 If the oxygen content range for the candidate fuel is 1.8 and 2.2, the candidate fuel and reference fuel oxygen value used in the predictive model equation is 2.0. For all other cases, see Table 6, Candidate and Reference Specifications for Oxygen.
- 3 The oxygen content (as MTBE) is reported because the hot soak evaporative benzene emissions model includes an MTBE content term (See VIII.A.2).
- 4 The oxygen content (as EtOH) is reported because the exhaust formaldehyde and the exhaust acetaldehyde models include EtOH content terms for the predictions for the candidate fuel specifications -(See VI.A.1.c & d., VI.A.2.c & d., VI.A.3.c & d.). The EtOH content term is not included in the exhaust formaldehyde and acetaldehyde predictions for the reference fuel specifications because it is assumed that, for the reference fuel specifications, MTBE is the oxygenate used to meet the oxygen requirement.
- 5 ~~If the applicant elects to use the evaporative HC emissions models, the flat RVP limit is 6.90. That is, all predictions for evaporative emissions increases or decreases are made relative to 6.90 psi. If the applicant has elected not to use the evaporative HC emissions models, the flat RVP limit is 7.00. The exhaust models contain an RVP term, but this term has been made constant by fixing the RVP for both the reference and candidate fuels at 7.00 psi in the calculation of the standardized RVP values used in the exhaust emissions equations. This fixing of the RVP takes RVP out of the exhaust models as a fuel property which effects exhaust emissions.~~
If the applicant wishes to certify a fuel containing ethanol, then the flat RVP limit is 7.00. If the applicant wishes to certify a fuel that does not contain ethanol, then the flat limit for RVP is 6.90 psi. In either circumstance, the cap limit for RVP is 7.20 psi. The exhaust models contain an RVP term, but this term has been made constant by fixing the RVP for both the reference and candidate fuels at 7.00 psi in the calculation of the standardized RVP values used in the exhaust emissions equations. This fixing of the RVP takes RVP out of the exhaust models as a fuel property which effects exhaust emissions.
- 6 The higher value is the small refiner CaRFG flat limit for qualifying small refiners only, as specified in section 2272.

Table 3 shows that the oxygen content is not specified in the CARBOB model by the user. The user specifies only the ethanol content of the finished gasoline, which is used in the CARBOB model equations to calculate the properties of the finished gasoline. As shown by the CARBOB model equations shown in Section 3, the ethanol content of the finished gasoline is used in all the CARBOB model equations except RVP.

The oxygen content of the finished gasoline is specified by the user when using either the Phase 2 or the Phase 3 predictive model. The user specifies in the predictive model an oxygen content range. The oxygen content range is specified when all other properties of the predictive model candidate fuel are specified, as shown in Table 4 above. For a more detailed discussion of the specification of the oxygen content range for predictive model candidate fuels, see the Predictive Model Procedures document.

After the CARBOB model predictions have been made and entered into the predictive model, all evaluations of the finished gasoline predictive model candidate fuel are made in accordance with the provisions of the Predictive Model Procedures.