Isobutanol Octane Blending Model with Gasoline

Cooperative Research and Development Final Report

CRADA Number: CRD-17-00689

NREL Technical Contact: Teresa Alleman

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Technical Report
NREL/TP-5400-78962
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Cooperative Research and Development Final Report

Report Date: January 13, 2021

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Gevo Inc.

CRADA Number: CRD-17-00689

CRADA Title: Isobutanol Octane Blending Model with Gasoline

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Sponsoring DOE Program Office(s):

USDOE Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office (BETO)

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$125,000.00
TOTALS	$125,000.00

Executive Summary of CRADA Work:

The purpose of this agreement between the National Renewable Energy Laboratory (NREL) and Gevo, under the DOE Small Business Vouchers Pilot, is to develop a predictive octane blending model for isobutanol and blendstocks for oxygenated blending (BOBs). Validated models of ethanol octane blending effects are currently used in refinery blending models. While it is known that isobutanol increases octane when blended into BOBs, the effect is non-linear, and dependent on hydrocarbon blendstock properties. Because no predictive model currently exists for isobutanol and BOBs, blenders must perform expensive and time-consuming tests to determine the octane effect on each batch of finished fuel.

NREL will make basic measurements of research octane number (RON) and motor octane number (MON) of finished gasoline-isobutanol blends prepared in a broad range of BOBs. The key properties and detailed composition of BOBs utilized will be measured by NREL. Using these measured fuel properties, NREL will develop a predictive octane blending model for isobutanol in BOBs that can be used by terminals to further reduce barriers to market penetration of isobutanol.

Summary of Research Results:

Current legislation allows 12.5 volume percent (vol%) and 16 vol% blending of isobutanol into gasoline blendstocks to produce finished fuels. One significant market barrier facing isobutanol blending is octane modeling of finished fuels. Although laboratory tests exist for research and motoring octane number (RON and MON, respectively), the use of an accurate and precise blending model has not been made publicly available. The goal of this project is to develop a blending model for octane of isobutanol-gasoline. Thirty-four gasoline blendstocks were blended with isobutanol at 12.5 vol% and 16 vol% and analytical properties were measured, including RON and MON, to evaluate the impact of isobutanol blending. Three models were developed based on these results: a linear molar blending model; a linear volumetric model; and a non-linear volumetric model. Comparison to measured analytical data showed the best fit with the non-linear volumetric model.

Complete details of the analysis and modeling are available in: Alleman, T.L.; Singh, A.; Christensen, E.D.; Simmons, E.; Johnston, G. "Octane Modeling of Isobutanol Blending into Gasoline", *Energy and Fuels* 2020, 34, 7, 8424-8431.
https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c00911

Task 1: Assist Company in procuring BOBs for blending with isobutanol.

NREL and Gevo collaborated to collect thirty-four (34) gasoline blendstocks for oxygenate blending (BOBs) for this project. The BOBs were analyzed using ASTM International (ASTM) test methods. Properties included in this analysis include RON (ASTM D2699), MON (ASTM D2700), detailed hydrocarbon analysis (DHA, ASTM D6729), vapor pressure (D5191), density (D4052), and distillation (D86).

BOBs were procured from around the U.S. and a wide variety of refiners and terminals. The range of BOB properties can be elucidated from the following figures. In Figure 1 illustrates the range of RON and MON for the BOB samples collected under the CRADA.

The variability in RON and MON is expected with samples collected from around the U.S. BOBs are produced to meet finished octane number requirements after blending with 10 vol% ethanol, which vary widely with geography, local requirements, and whether the finished fuel is branded as a "regular" or "premium" gasoline.

Table 1 shows the geographic region where each sample was produced, based on petroleum area defense district. Note that production region does not necessarily indicate the region where the finished fuel will be sold.

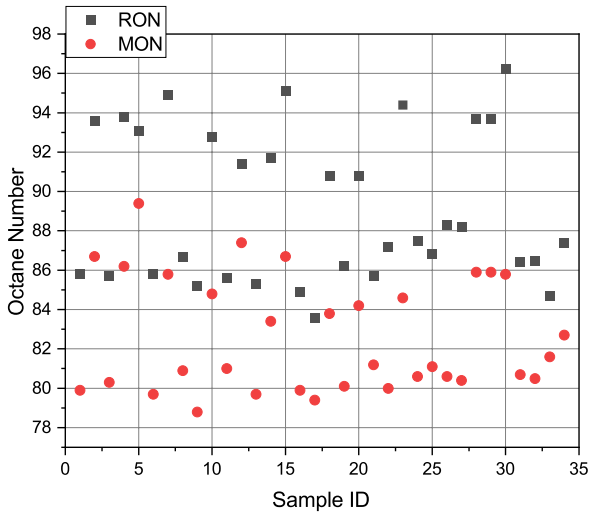

Figure 1. RON and MON analysis results for BOBs used in this project.

Table 1. Geographic region where BOBs were produced based on Petroleum Area Defense District

PADD 1	PADD 2	PADD 3	PADD 4	PADD 5	TOTAL
2	11	7	8	6	34

Figure 2 illustrates the distillation curves of the BOBs used in this project. The RVP and specific gravity of the BOBs is shown in Figure 3. Note that the majority of samples used in this project are summertime BOBs, though a few wintertime samples, as noted by the higher RVP, are also included.

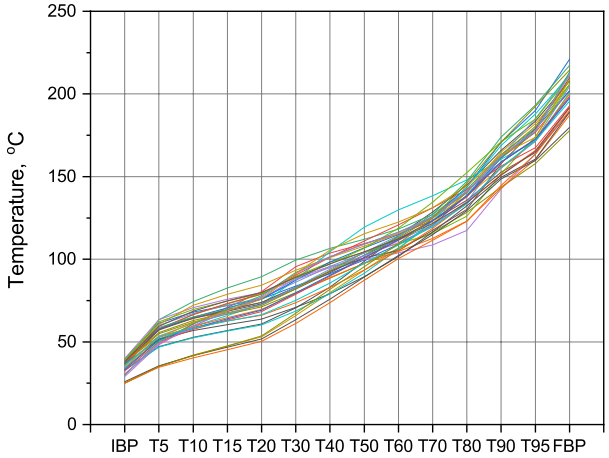

Figure 2. Distillation curves for BOBs

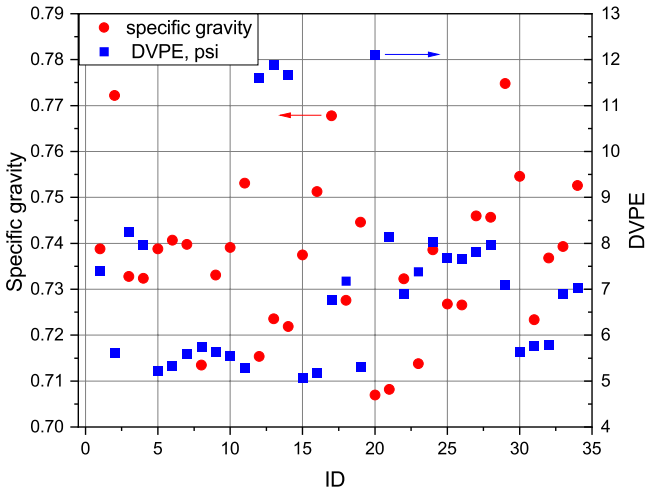

Figure 3. RVP and specific gravity of BOBs. Specific gravity is on the left axis and DVPE is on the right axis.

The DHA analysis is used to analyze each compound contained in the BOBs for this study. Due to the large number of potential compounds, data is presented as classes: paraffin (P), isoparaffin (I), olefin (O), naphthene (N), and aromatic (A) content. The ranges for each compound class are also presented in Table 2.

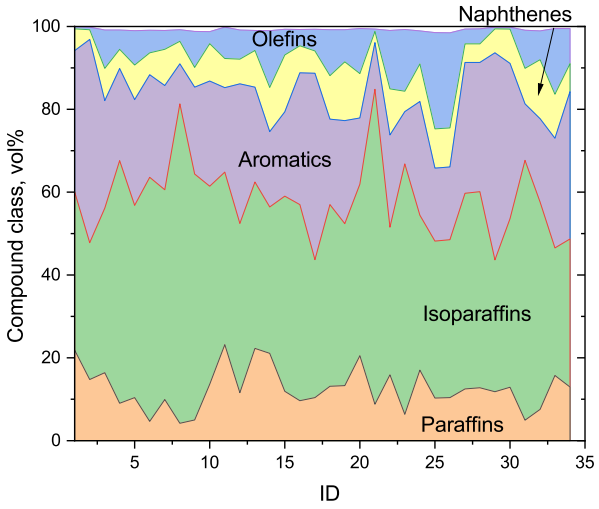

Figure 4. PIONA compound classes for BOBs

Table 2. Ranges of PIONA classes for BOBs

	Paraffins (vol%)	Iso-paraffins (vol%)	Olefins (vol%)	Naphthenes (vol%)	Aromatics (vol%)
Min.	**4.2**	**30.8**	**0.35**	**2.28**	**9.61**
Max.	**23.2**	**77.1**	**23.2**	**14.3**	**50.0**
Average	**12.6**	**45.6**	**7.58**	**7.81**	**25.6**
Median	**12.2**	**41.5**	**6.98**	**8.01**	**24.8**

Task 2: Blend isobutanol into each BOB and measure octane

NREL targeted blends of 12.5 vol% and 16 vol% isobutanol in each BOBs. Isobutanol was provided by Gevo from their Luverne, MN plant. Samples were chilled to approximately 4°C and blended gravimetrically by hand. The RON, MON, RVP, and isobutanol content of the finished blends were measured. The subsequent tasks used the measured isobutanol content, so blends were only produced once and no effort was made to refine isobutanol content.

The isobutanol content in the blends was measured with gas chromatography (GC) using a two-dimensional heart-cutting technique. The GC was an Agilent 7890A with a Deans switch and dual flame ionization detectors. The polar column was a DB-1 (30m x 0.25 mm, 0.25 mm df) and the non-polar column was a DB-Wax (30m x 0.25 mm, 0.25 mm df). A 0.77m x 0.1mm deactivated silica restrictor was used to connect the DB-1 from the Deans switch to the detector. The initial oven temperature was 70 °C with a 2-minute hold, followed by a 20 °C/min ramp to a final temperature of 230 °C. The injector and both detectors were held at 250 °C. Samples were injected as 1 mL volume with a 200:1 split ratio. A six-point gravimetric calibration was developed using isobutanol in heptane with an R^2 of 0.999.

It was expected that hand blends would be less accurate than blends produced at the terminal and this is confirmed by Figure 5. The RON and MON for the finished blends are shown in Figure 6. The impact of blending isobutanol on the RVP was below the reproducibility of the test method, in most cases, and the data is not presented here.

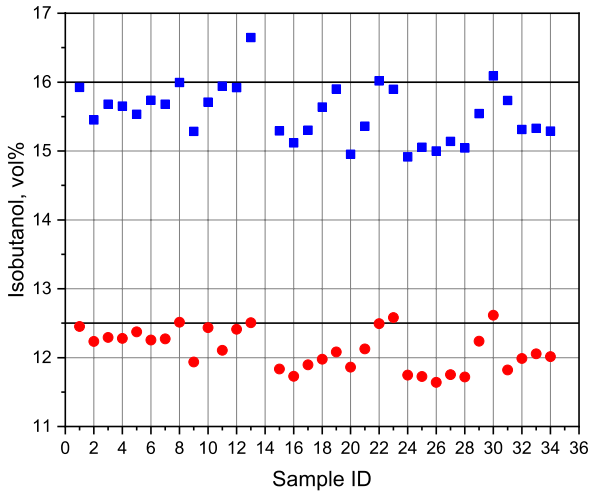

Figure 5. Measured isobutanol content of finished blended fuels

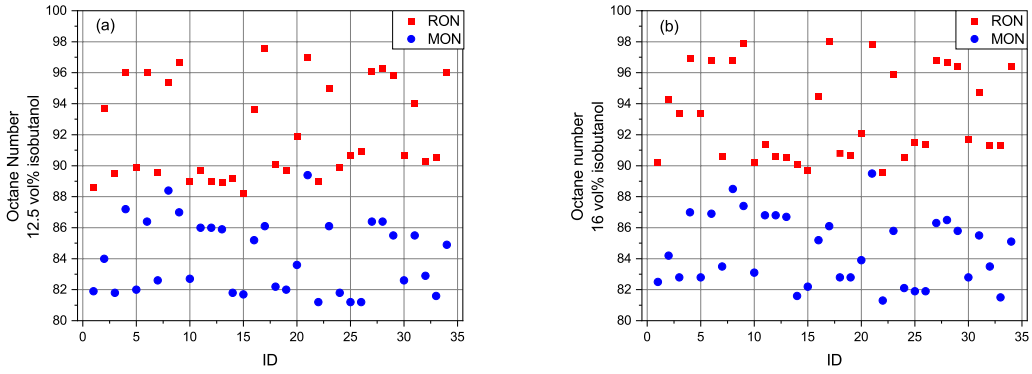

Figure 6. RON and MON of isobutanol-BOB blends. (a) 12.5 vol% isobutanol content. (b) 16 vol% isobutanol content.

Task 3: Develop a predictive octane blending model for isobutanol-BOB blends

Significant literature exists discussing the impact of blending alcohols into BOBs and the resulting octane number (1-4). Oxygenates are well known to cause non-linear blending effects and some models use a "blending" octane number, although that approach was not taken in this study due to the complexity of interactions with the hydrocarbons in the BOBs (5-11). Previous work has shown that linear volumetric models were not sufficiently accurate to predict the RON of isobutanol blends (6,12). Anderson et al. modeled ethanol-BOB blends using a molar blending correlation, which produced a nearly linear relationship (7).

The basis for the modeling in this work was based on the work of Ghosh et al. (1). In their work, two predominant techniques are used to predict octane number: deriving the finished octane number based on individual components or measuring the octane number of individual components in the fuel. The work by Ghosh et al. (1) developed a model to predict octane number using the composition of gasoline and included non-linear interactions from the oxygenates.

Three predictive models were developed for modeling the octane response of isobutanol-BOB blends a linear volumetric model, a linear molar model, and a non-liner volumetric model. The volumetric model followed equation (1),

$$\boldsymbol{ON_{Blend} = v_{BOB} ON_{BOB} + v_{iBu} ON_{iBu}} \quad (1)$$

where ON is the RON or MON of the finished blend, BOB, or isobutanol, n is the volumetric fraction of the BOB and isobutanol in the finished blend.

The linear molar model follows a similar format, using the assumption that isobutanol and BOBs blend linearly for octane number. The molar model is shown in equation (2), where x is the molar fraction of the BOB and isobutanol in the finished blend. Using the DHA results, the average molecular weight of the BOBs can be estimated, and moles of BOB calculated.

$$\boldsymbol{ON_{Blend} = x_{BOB} ON_{BOB} + x_{iBu} ON_{iBu}} \quad (2)$$

The third model, a nonlinear volumetric one, assumes non-linear blending behavior of isobutanol with the BOBs. Our model deviated from previous models in that the octane number of the BOBs was known (instead of estimated) and used in the model development. The model follows equation (3),

$$\boldsymbol{ON_{Blend} = v_{BOB} ON_{BOB} + v_{iBu} ON_{iBu} + \sum_{j=PIONA} \left(\frac{k_{iBu,j} v_j v_{iBu} ON_{iBu}}{1 + k_{iBu,j} v_j} \right)} \quad (3)$$

Similar to equations (1) and (2), ON is the octane number, either RON or MON, of the finished blend, BOB, or isobutanol. The volume of BOB and isobutanol in the blend, **n,** is also included. This model uses the contributions of the various PIONA fractions calculated by the DHA and assumes a linear interaction with the isobutanol and each hydrocarbon group for simplicity.

The models were fit by randomly partitioning the BOBs into a training set and testing set using a k-fold method. Further details of the modeling are in the technical paper. The modeling accuracy is +/- 1 ON.

Modeling results for the simple volumetric model are presented in Figure 7, comparing measured ON with predicted ON from the model. The impact of blending isobutanol appears to have a larger impact on RON, than MON, and increased deviation from linearity as isobutanol concentration increases.

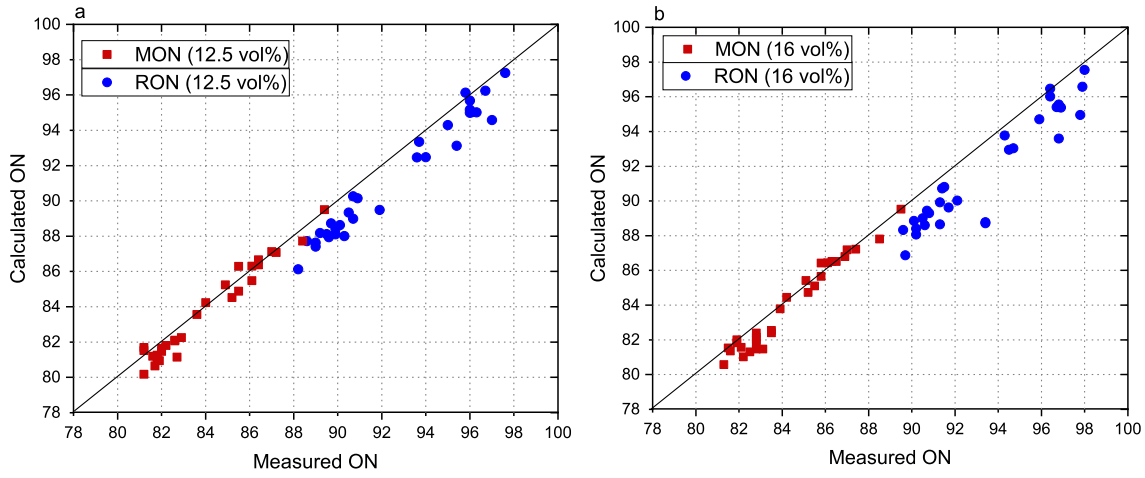

Figure 7. Calculated RON and MON, based on the linear volumetric blending model for isobutanol–gasoline mixture at (a) 12.5 vol% blends, and (b) 16 vol% blends

The simple molar model improved the ability to estimate RON and MON compared to the volumetric model. Some deviation was still observed at higher isobutanol concentrations compared to lower concentrations (Figure 8).

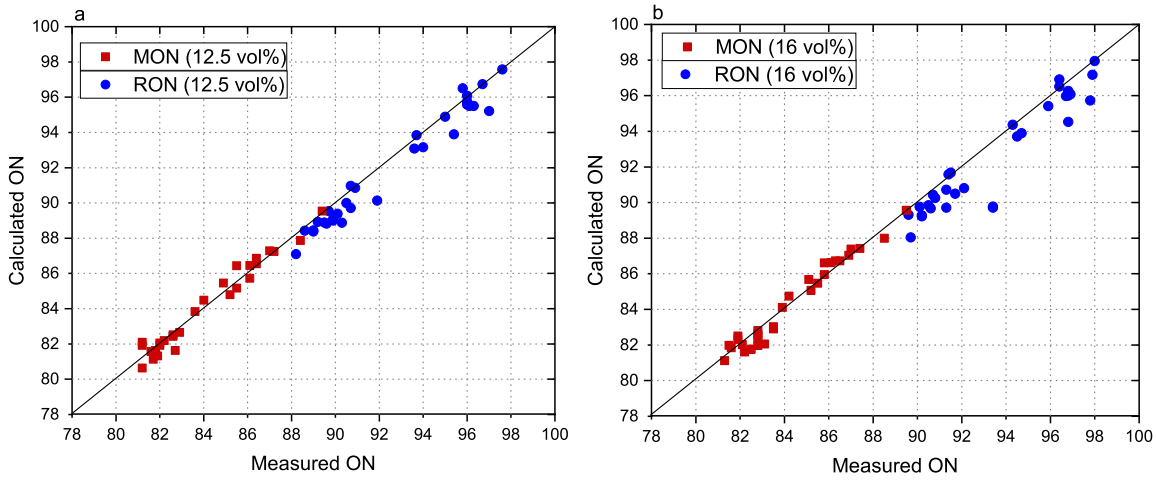

Figure 8. Calculated RON and MON, based on the linear molar blending rule for isobutanol

The non-linear volumetric model provided the best fit for estimating RON and MON of isobutanol-BOB blends. Values of k in equation (3) were optimized to predict RON and MON (further details may be found in the technical paper). A summary of k is presented in Table 3 for each compound class. The sign of K indicates whether a synergistic (positive) or antagonistic (negative) interaction exists for each compound class.

Table 3. Interaction coefficients of isobutanol with hydrocarbon composition groups as derived from the nonlinear blending model, equation (3).

	ON	kiBu,P	kiBu,I	kiBu,O	kiBu,N	kibu,A
12.5 vol% isobutanol	RON	0.52	0.21	-0.42	0.87	-0.27
	MON	0.37	0.08	-0.45	0.78	-0.25
16 vol% isobutanol	RON	0.53	0.23	-0.38	0.64	-0.22
	MON	0.35	0.05	-0.38	0.78	-0.20

Larger k values indicate more significant interactions with RON and MON from the hydrocarbon classes identified by the DHA. The strongest synergistic effect on RON and MON is due to naphthenic content of the BOBs, though the average naphthenic content of these samples was 8 vol%. The paraffinic content, averaging 12 vol% in the samples, also blended synergistically. The isoparaffins, which are the main hydrocarbon identified in the samples (41 vol% on average), had a minimal effect on MON and a limited effect on RON. Aromatics and olefins had antagonistic effects on RON and MON and accounted for 25 vol% and 7 vol%, on average, of the samples, respectively. The closeness of the measured and predicted RON and MON for the non-linear model is illustrated in Figure 9.

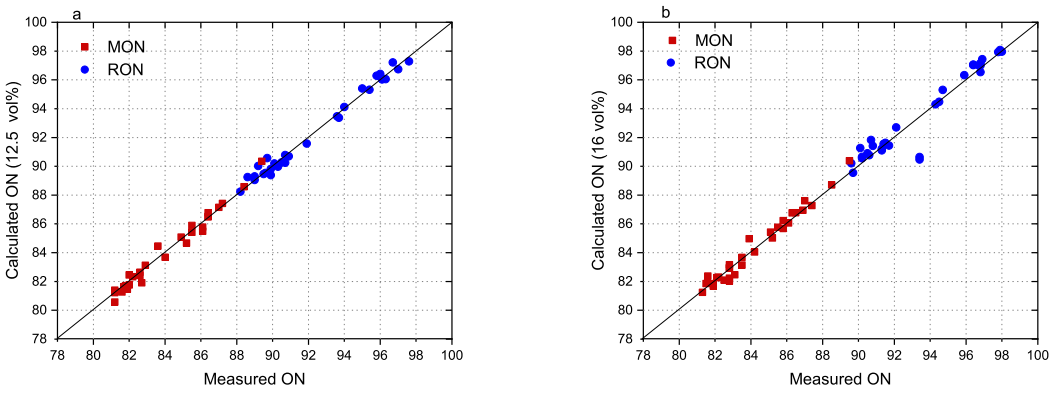

Figure 9. Predicted RON and MON based on the nonlinear model for interaction of isobutanol with hydrocarbon groups for (a) 12.5 vol% blends, and (b) for 16 vol% blends.

Summary Conclusion:

Thirty-four BOBs were collected from around the U.S. Each BOB was analyzed for a variety of properties, including RON, MON, RVP, and DHA. The samples were deliberately weighted toward summertime BOBs, with low RVPs. Finished blends were hand produced by blending each BOB with 12.5 vol% and 16 vol% isobutanol. The finished fuels were reanalyzed for RON, MON, and RVP.

Three models were developed to predict RON and MON of the finished blends. The models were a linear volumetric model, a linear molar model, and a non-linear volumetric model. The best prediction of finished blend ON was found using the non-linear volumetric model. This model

found synergistic blending behavior for paraffins and napthenes in the BOBs and antagonistic behavior from the aromatics and olefins. The goodness of fit for the non-linear volumetric model was approximately +/- 1 ON.

This work was based heavily on detailed analytical properties measured for each BOB. Future work is recommended to improve these models with more realistic properties readily available at terminals were isobutanol is blended with BOBs.

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Subject Inventions Listing:

None

ROI #:

None