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Product Value Modeling for a Natural Gas Liquid to Liquid Transportation Fuel Process

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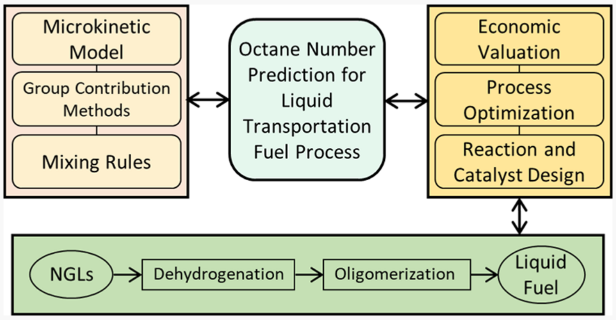

ABSTRACT: Light alkanes from shale resources can potentially be converted to an easy-to-transport liquid hydrocarbon product by catalytic dehydrogenation followed by catalytic oligomerization. The chemical species in the liquid product and their concentrations depend on the process design, operating conditions, and choice of catalyst(s). In order to optimize process design and catalyst selection, it is important to be able to evaluate the economic value of the liquid product stream as a function of design variables and operating conditions. As an initial effort in addressing this challenge, the mixture octane number, a key property in determining the value of a gasoline blend stock, is considered. An approach is outlined for the estimation of the mixture octane number using a functional group contribution method and appropriate mixing rules, and this estimation procedure is interfaced with a microkinetic oligomerization reactor model. This combined microkinetic and octane number modeling approach is demonstrated using two case studies involving ethylene and propylene as feed streams, with product streams characterized in terms of octane number, molecular size distribution, and degree of branching. Results of this type are expected to provide guidance on catalyst development and process optimization.

1. INTRODUCTION

Despite recent developments in renewable energy technologies, in the first quarter of 2019 about 81% of the energy demand in the United States was fulfilled by fossil fuels.[1] Natural gas was the most rapidly growing source over the past decade, due to advances in producing gas from shale formations. The U.S. Energy Information Administration (EIA) estimates that the United States has about 308 trillion cubic feet (Tcf) of proved shale gas resources.[2] In addition to this, the latest, year-end 2016 assessment[3] from the Potential Gas Committee (PGC) suggests that the United States has 2817 Tcf of unproved technically recoverable natural gas resources, of which shale accounts for 1797 Tcf (64%). According to the EIA,[4] shale gas production in 2018 was about 18 Tcf (dry basis), with a mean projected 2050 value of about 33 Tcf. This represents[4] approximately 62% of total gas production in 2018 with a mean projected increase to 77% of total gas in 2050. To meet the energy demands of the 21st century, the United States is becoming increasingly dependent on shale gas.

Unlike conventional natural gas, shale gas typically contains significant amounts of light hydrocarbons other than methane, such as ethane, propane, and butanes. The amount and composition of such “natural gas liquids” (NGLs) may vary substantially from one production region to another.[5] In 2018, NGL production[4] in the United States was 4.3 million barrels/day (MMBD), with a mean projected increase to 6.0 MMBD by 2030. The pipeline infrastructure to transport NGLs, however, often does not exist in new and remote shale gas regions, leading to processing inefficiencies and loss of resources, including via flaring. Research and strategic innovation in shale gas processing will prove crucial to maximizing the use of U.S. shale gas resources. For example, Ridha et al.[6] have suggested an NGL-to-liquid conversion process, with the goal of facilitating modular, close-to-wellhead conversion of NGL to liquid transportation fuel and mitigating resource losses. In this process, the NGL alkanes are activated by catalytic dehydrogenation to alkenes, followed by a catalytic oligomerization process to hydrocarbons in the gasoline range. In order to design and optimize an NGL-to-liquids or NGL-to-fuels process, a means for determining an economic value for the liquid fuel product and its dependence on oligomerization process conditions, such as type and loading of catalyst, reactor temperature, pressure, and reactor feed composition, is needed.

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This paper describes and demonstrates a procedure for accomplishing this.

To describe the oligomerization reactor, a recently developed microkinetic model[7] is employed to predict product stream compositions based on catalyst selection, reaction, and feed stream conditions. Depending on the level of complexity of the model, the product stream may include a very large number (hundreds, or even thousands) of individual chemical species. Assuming that the target use for the liquid oligomerization product is as a gasoline blend stock, a key metric in determining its economic value is the octane number (ON), a measure of resistance to engine knocking in spark-ignited internal combustion engines. Wilson and Turaga[8] have studied the value of an octane barrel over the period 2010−2015 and found that it trended upward in all U.S. regions. However, the rate of increase depended on the region. For example, in 2015, the value of an octane barrel in the Midwest was about \$4.7 ON^{-1} bbl^{-1} and about \$2.7 ON^{-1} bbl^{-1} on the West Coast, whereas in 2010, the value throughout the United States was about \$2 ON^{-1} bbl^{-1}. To enable use of the ON metric for economic evaluation of the oligomerization product, a method is described in this paper for estimating the ON for mixtures involving a very large number of components. This approach combines a group contribution approach[9] for pure-component ONs with an equation of state (EOS) inspired mixing rule[10] to obtain the mixture ON.

The approach described in this paper enables the consistent and equitable comparison of hydrocarbon mixtures on an economic basis and can thus be used in the optimization of oligomerization reaction conditions. It can also serve to identify desirable or undesirable oligomerization products and consequently inform the tuning of reaction pathways through catalyst design. This is illustrated via case studies based on oligomerization of propylene and ethylene feed streams. Ultimately, the approach demonstrated here can be used to guide process development research efforts to high-value hydrocarbon products.

This paper is organized as follows. In section 2, a brief overview of the microkinetic model used for the oligomerization reactor is provided. Then, in section 3, a procedure for estimating the ON of the oligomerization product mixture, using a structural group contribution method and EOS-based mixing rules, is described. Next, in section 4, the combined microkinetic and ON modeling approach is demonstrated using two case studies. Finally, concluding remarks are given in section 5.

2. OLIGOMERIZATION MICROKINETIC MODEL OVERVIEW

In this paper, a combined microkinetic and octane number modeling approach is described for economic evaluation of an oligomerization reactor product. While this approach can be applied in connection with any appropriate microkinetic oligomerization reactor model, the microkinetic model previously developed by Vernuccio et al.[7] for the oligomerization of light alkenes over a ZSM-5 catalyst was used here. The model determines the molecular composition of the reactor output as a function of operating conditions such as temperature, pressure, feed flow rate, and mass of catalyst. A brief overview of the model is presented below.

Microkinetic models aim to represent all mechanistic elementary steps and intermediates involved in a chemical reaction. Compared to lumped kinetics, these tools offer a more fundamental understanding of the molecular processes occurring inside ZSM-5 pores and at the catalyst surface. In Vernuccio et al.,[7] the surface chemistry of the process was described by using a set of eight reaction families (protonation, deprotonation, oligomerization, β-scission, methyl shift, hydride shift, α-PCP-branching, β-PCP-branching). The ionic intermediates can also undergo hydride transfer steps to form paraffins; however, a relatively negligible amount of paraffins are formed as validated by Vernuccio et al.[7] at low conversion (<4%) of propylene using experimental data. In order to limit the size of the network, these hydride transfer reactions were not included. The physisorption of the gas phase olefins and the desorption of the corresponding species from the pores of the zeolite were taken into account.

A reaction network was constructed by using an automated network generator.[11] In this generation process, molecular and ionic species were represented using bond and electron (BE) matrices, based on their given graph representations. The off-diagonal entries *ij* of the matrices provide the connectivity and bond order of atoms *i* and *j*. Two example BE matrices, for a primary propoxide and a secondary propoxide, are depicted in Figure 1. To describe a reaction, reduced BE matrices are first constructed based on the consideration that only some of the atoms of the reacting molecular or ionic species are participating in the reaction. This allows the identification of a reaction operator representing the difference between reactant and product, as depicted in Figure 1 for an example hydride shift. By adding the reaction operator to the reduced BE matrix of the reactant, the reduced BE matrix of the product is generated. Following this approach, a reaction operator was defined for each reaction family involved in the oligomerization process.

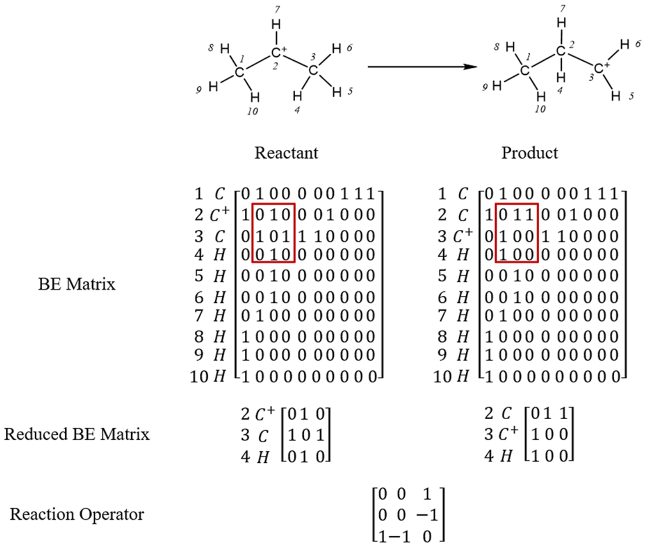

Figure 1. Development of the hydride shift reaction operator. Atoms in reactants and products are numbered and converted into BE matrices. Reduced BE matrices are identified considering the atoms that effectively participate in the reaction. The reaction operator is obtained as a difference of product and reactant reduced BE matrices.

The reaction network was automatically generated by applying the reaction operators to the reactants and their progeny, resulting in 909 species (269 gas-phase molecules, 269 physisorbed molecules, and 371 ionic intermediates) and 4243 elementary reactions. In order to efficiently terminate the generation procedure, only propylene, ethylene, and the ionic intermediates with less than 10 carbon atoms were allowed to react. However, the microscopic reversibility of the network was ensured by coupling every reaction operator with its corresponding reverse reaction.

The reaction rates r_i for every species i included in the network were expressed in the form

$$r_i = \sum_j \pm A_j \exp\left(-\frac{E_{aj}}{RT}\right)\prod_k C_k \tag{1}$$

following an Arrhenius temperature dependence. Here A_j is the frequency factor for reaction j, R is the universal gas constant, T is the temperature, E_{aj} is the activation energy for reaction j, and C_k is the partial pressure of a molecular species k or the fractional coverage of an ionic intermediate k. The sign of each term j in the summation is determined by whether species i is a product (plus sign) or reactant (minus sign) in reaction j.

The frequency factors were estimated using transition state theory[12] based on the entropy changes between reactants and correspondent activated complexes that are tabulated in the literature.[13] According to the Evans–Polanyi relationship,[14] the activation energies were expressed as linear functions of the enthalpy change ΔH_R associated with an elementary step:

$$\begin{aligned} E_a &= E_0 + \alpha\Delta H_R \quad \text{for } \Delta H_R \le 0 \\ E_a &= E_0 + (1-\alpha)\Delta H_R \quad \text{for } \Delta H_R > 0 \end{aligned} \tag{2}$$

where E_0 is the intrinsic energy barrier and α is the transfer coefficient ($0 \le \alpha \le 1$) that characterizes the position of the transition state along the reaction coordinate. The reaction enthalpy of every elementary step can be expressed as

$$\Delta H_R = \Delta H_{R,g} + \sum_i \nu_i \Delta q(R_i^+) + \sum_i \nu_i \Delta H_{phys}(RH_i) \tag{3}$$

where R_i^+ and RH_i represent, respectively, a generic ionic intermediate and a generic molecular species, ν_i is the stoichiometric coefficient of each species i in the elementary step and is defined as positive for products and negative for reactants, $\Delta H_{R,g}$ is the reaction enthalpy in the gas phase calculated based on Benson's group additivity method,[15] $\Delta q(R_i^+)$ is the stabilization enthalpy[13] of ionic intermediate R_i^+, and $\Delta H_{phys}(RH_i)$ is the enthalpy change of neutral molecular species RH_i in going from the gas phase to its physisorbed state within the zeolite pore.[16,17]

The expressions of the elementary reaction rates were incorporated into the design equation of a plug flow reactor resulting in a system of 909 ordinary differential equations that was associated with the mass balance for the surface coverage and numerically integrated to determine the molecular composition of the reactor output. For the case studies presented below, simulations were conducted using propylene as a reactant under varying temperatures (483–522 K), space velocities (0.8–9.2 $\text{mol}_{C_3}(\text{mol}_{H^+})^{-1}\ \text{s}^{-1}$), and feed compositions (propylene vs ethylene). Under these conditions, a wide range of alkene conversion values can be observed. Since the Vernuccio et al.[7] model and its assumption of negligible paraffin content in the overall product distribution was validated experimentally only for low (<4%) propylene conversion, a more complex version of the model that includes the presence of paraffins in the product distribution was developed and tested to ensure the applicability of the model to calculate ON at higher conversions, though, in this regard, the literature is rich in examples where paraffins are neglected during olefin oligomerization and cracking processes on acidic zeolites.[18−20] The generation of paraffins was captured by including in the reaction network hydride transfer between olefins and ionic intermediates as an additional reaction family. Despite the significantly larger network, the inclusion of these additional elementary steps in the microkinetic model resulted in product ON changes lower than 1.2%, due largely to the low paraffin content of the product. For this reason, the smaller reaction network, without paraffin formation, was used in the case studies. For more general circumstances, the larger network, including paraffins, may need to be used.

3. OCTANE NUMBER CALCULATION

Octane number is typically measured by two recognized laboratory test standards. The "research method" standard (ASTM D2699) defines the research octane number (RON), which is measured at relatively light engine loading, characteristic of city driving or highway cruising. The "motor method" standard (ASTM D2700) defines the motor octane number (MON) which is measured at relatively heavy engine loading, characteristic of hard acceleration or sustained uphill driving. The problem of estimating the RON and/or MON of a mixture of components, whether molecular species, distillation fractions, or other blending components, is well studied. For the case of a mixture of molecular species, such as the oligomeriztion reactor effluent predicted by the microkinetic model, there are several methods available, as reviewed by Twu and Coon,[10] Knop et al.,[21] and Stratiev et al.[22] With some exceptions,[21] these methods represent the ON of a mixture as some nonlinear function of the pure-component ONs and the liquid-phase volume fractions of the components, with parameters fitted to experimental data. For the mixtures of interest here, there are a very large number of molecular components present, out of which only a relatively small number of experimentally measured values of pure-component ONs are available. Thus, it is necessary to estimate many pure-component ONs based on the molecular structures of the components.

After evaluation of the available options, the following estimation model was developed for calculation of mixture ON. First, given the molecular structures of the individual components, each is decomposed into its functional groups. Knowledge of the functional groups is then used in group contribution methods applied to each species in the mixture to obtain pure-component properties. For pure-component ONs, the method of Albahri[9,25] is used, and for pure-component liquid molar volumes (needed to determine volume fractions), the method of Constantinou et al.[23] is used. When available, data[24] for pure-component ON and pure-component liquid molar volume are used in place of the aforementioned methods. Finally, these pure-component properties are used with the nonlinear mixing rules of Twu and Coon[10] to calculate an estimate of the mixture ON. A flowchart of this procedure is shown in Figure 2. Details of this procedure are provided in sections 3.1 and 3.2.

3.1. Pure-Component Octane Number.

Albahri[9,25] has described a structural group contribution model to calculate the pure-component octane numbers (RON and MON) for a given compound. For species k, the equation

$$\text{ON}_k^0 = a + bS_k + cS_k^{\,2} + dS_k^{\,3} + eS_k^{\,4} + f/S_k \tag{4}$$

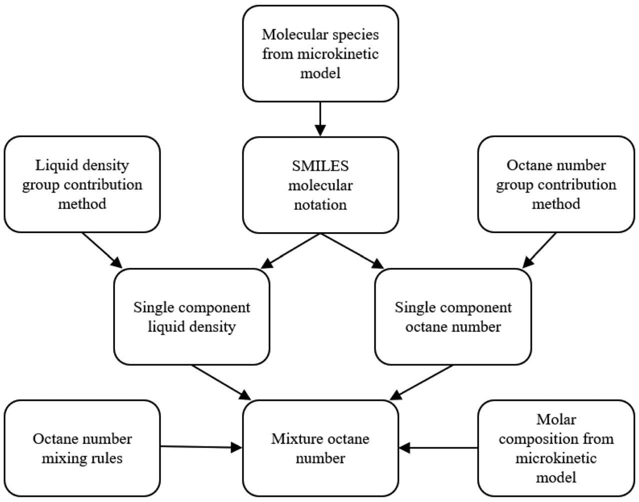

Figure 2. Mixture octane number estimation model flowchart.

with S_k indicating the sum over groups

$$S_k = \sum_i n_{ki}(\mathrm{ON})_i \tag{5}$$

is used. Here ON_k^0 can represent either the pure-component RON or MON of species k, n_{ki} is the number of occurrences of structural group i in species k, and ON_i is the contribution of structural group i from Table 1. The coefficients a, b, c, d, e, and f (valued differently for RON and MON) were determined from experimental data for over 200 hydrocarbon liquids covering a wide ON range (−20 to +120) and are given in Table 2. For the set of structural groups shown in Table 1, the average deviation between experimental and predicted ON was 5.0 for RON and 5.7 for MON. Albahri[9,25] also considered using a larger set of structural groups, which slightly improved RON prediction (average deviation 4.0) but resulted in poorer MON prediction (average deviation 7.9).

Table 1. Group Contributions for Estimation of Pure-Component Octane Numbers[9,25]

HC type	group	$(\mathrm{RON})_i$	$(\mathrm{MON})_i$
paraffins	$-CH_3$	−2.315	−0.202
	$>CH_2$	−8.448	−9.082
	$>CH-$	−0.176	−1.821
	$>C<$	11.94	11.90
olefins	$=CH-$	0.392	−2.293
	$>CH=$	8.697	2.703
	$=CH_2$	3.623	−0.254
	$=C=$	−37.37	−42.43
	$\equiv CH$	18.36	21.36
	$\equiv C-$	−7.201	−12.96
cyclic	$>CH_2$	−4.421	−5.377
	$>CH-$	−2.177	−3.631
	$>C<$	8.916	10.52
	$=CH-$	2.879	−4.765
	$>C=$	5.409	5.065
aromatic	$=CH-$	3.591	9.725
	$>C=$	2.382	−5.650

Table 2. Coefficients Used in Group Contribution Method for Pure-Component Octane Numbers[9,25]

octane no.	a	b	c	d	e	f
RON	103.6	0.231	−0.0226	0.001	1.42×10^{-5}	1.58
MON	87.3	0.272	-4.78×10^{-3}	2.73×10^{-4}	-2.8×10^{-6}	−0.1058

The process effluent stream from the microkinetic model of the oligomerization reactor is a blend of hundreds of hydrocarbon compounds. For the majority of these, experimental values of the pure-component ON are not available. When available, experimental data for pure-component RON and MON are used.[24] When unavailable, and due to the large number of pure-component ON estimates needed, an automated computational procedure is employed to identify functional groups. For this purpose, the chemical species in the process effluent stream are first identified by the simplified molecular-input line-entry system, commonly referred to as SMILES notation.[26−28] SMILES represents a form of line notation that describes the chemical structure of a compound using ASCII characters arranged in short strings. The structural groups for all pure components in the effluent stream are then identified from their respective SMILES strings to calculate their respective pure-component ONs.

3.2. Mixture Octane Number.

To estimate the ON of a liquid mixture, the method of Twu and Coon[10] is used. This is a semiempirical approach in which mixing rules are derived based on equation-of-state arguments, but with binary interaction parameters, based on compound type, fitted to experimental data. The mixing rules used are given by[10]

$$\mathrm{ON} = \sum_i \sum_j z_i z_j a_{ij} \tag{6}$$

$$a_{ij} = \frac{1}{2}(\mathrm{ON}_i^0 + \mathrm{ON}_j^0)(1 - K_{ij}) \tag{7}$$

where ON is the mixture octane number (MON or RON), ON_i^0 and ON_j^0 are the pure-component octane numbers (MON or RON) of species i and j respectively, and z_i and z_j are the volume fractions of species i and j respectively. The parameter K_{ij} is a universal binary interaction parameter based on the types (olefinic, aromatic, or saturate) of species i and j, as shown in Table 3. If the types of species i and j are the same, then $K_{ij} = 0$. The values of K_{ij} were fitted by Twu and Coon[10] to data for 161 mixtures from 157 gasoline cuts with an overall average absolute deviation percent of 1.00% for RON and 1.19% for MON.

Table 3. Universal Binary Interaction Parameters for Mixture Octane Numbers[10]

octane no.	interaction	K_{ij}
RON	olefinic−aromatic	0.0670
	olefinic−saturate	−0.1021
	aromatic−saturate	−0.0232
MON	olefinic−aromatic	0.0354
	olefinic−saturate	−0.0800
	aromatic−saturate	0.0271

The microkinetic model generates the molar composition of all the components, which must be converted to the volume

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fractions z_i for use in the mixing rule equations (6) and (7). Therefore, another group contribution method is employed to determine the liquid molar volume of each pure component, which is then used to convert the molar composition to volumetic composition. The same automated functional group identification procedure based on SMILES notation and used for the ON group contribution method is employed. When available, experimental data for pure-component liquid molar volume is used instead of the group contribution estimate.[24]

The molar volume is calculated by the method of Constantinou et al.[23] Here, only the first-order group contributions are considered, so the method is expressed by[23]

$$V_k = d + \sum_i n_{ki} v_i \tag{8}$$

where V_k is the pure-component liquid molar volume for species k in m^3 $kmol^{-1}$, d is a constant equal to 0.01211 m^3 $kmol^{-1}$, n_{ki} is the number of functional groups i in species k, and v_i is the contribution of group i in m^3 $kmol^{-1}$ from Table 4. Note that the group definitions are slightly different from those used in the ON group contribution method.

Table 4. First-Order Group Contribution for Estimation of the Liquid Molar Volume[23]

HC type	group	v_i (m^3 $kmol^{-1}$)
paraffins (including cyclic)	$-CH_3$	0.02614
	$>CH_2$	0.01641
	$>CH-$	0.00711
	$>C<$	−0.00380
olefins (including cyclic)	$CH_2{=}CH-$	0.03727
	$-CH{=}CH-$	0.02692
	$CH_2{=}C<$	0.02697
	$-CH{=}C<$	0.01610
	$>C{=}C<$	0.00296
	$CH_2{=}C{=}CH-$	0.04340
	$-C{\equiv}CH$	0.01451
	$-C{\equiv}C-$	0.01451
aromatic	$=CH-$	0.01317
	$>C{=}$	0.00440

The results obtained from the ON estimation model described above were compared to three-component experimental results[29] compiled for 26 mixtures of 32 vol % *n*-heptane (RON = MON = 0 by definition), 48 vol % isooctane (2,2,4-trimethylpentane; RON = MON = 100 by definition), and 20 vol % of another species. The third, variable species includes saturates, olefins, and aromatics with vastly different pure-component ONs. Figure 3 shows a comparison of the predicted and measured RON and MON for each of the 26 mixtures, indicating good agreement. An average absolute percentage deviation of 1.8% for RON and 1.7% for MON between the model predictions and the literature values was obtained. None of these experimental data were used in fitting the parameters used in the estimation procedure.

4. CASE STUDIES

Two case studies are presented here to demonstrate the application of the combined microkinetic and ON modeling approach for evaluating an oligomerization reactor product stream. Since the conversion of light olefins to liquid products in the oligomerization reactor is not complete in these studies, a vapor−liquid separation of components in the reactor effluent is needed,[6] with the vapor stream possibly recycled, and the liquid phase representing the main product of interest. It is assumed here that a sharp separation between C_4 and C_5 hydrocarbons is achieved. Thus, the liquid product of interest is assumed not to contain any C_4 or lighter species, and these species do not contribute to the product ON in these case studies. Though it is not considered here, another key property in evaluating a potential gasoline blend stock, and which also depends on the degree of the C_4−C_5 separation, is its volatility (typically expressed in terms of the Reid vapor pressure). A final gasoline blend must meet volatility constraints, which vary geographically and seasonally. The ON modeling approach described here can be used in connection with any degree of vapor−liquid separation.

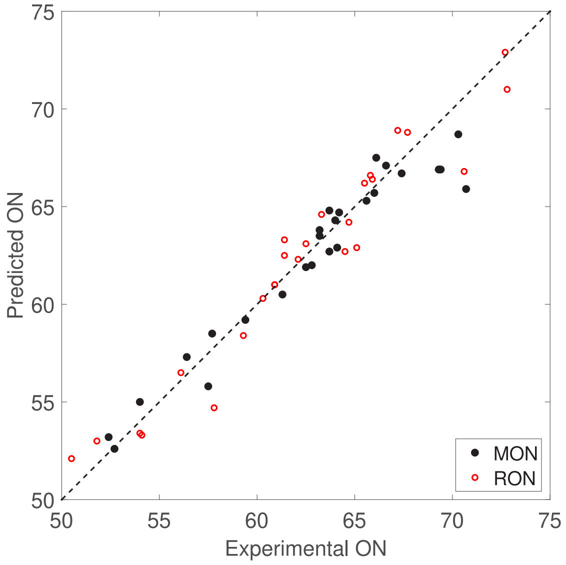

Figure 3. Predicted vs measured values for RON and MON for 26 ternary mixtures. This represents an average absolute percentage deviation between predicted and measured values of 1.8% for RON and 1.7% for MON.

4.1. Propylene Oligomerization.

As a case study, the impact of various propylene oligomerization reaction conditions on reactor effluent stream ON was considered. Using the microkinetic model, effluent composition was recorded for various reactor parameters including catalyst loading, molar flow rate, and temperature. Subsequently, the effluent mixture ON was calculated for each scenario. Figures 4 and 5 illustrate the relationship found between ON and conversion for this application. Here, conversion is defined based on the propylene molar flow rate reduction across the reactor, as given by the microkinetic model; it depends on the values used for molar flow rate, catalyst loading, and temperature. For this particular case study, it was found that ON was not highly sensitive to changes in the reactor parameters studied. ON decreases slightly with increasing molar flow rate and increases slightly with increasing catalyst loading. Consequently, ON generally increases with respect to reactor residence time and hence conversion. However, in higher conversion scenarios, MON is observed to reach a maximum with respect to conversion, especially for the higher temperature cases. For RON, a maximum is not observed, but for the higher temperature cases, the rate of increase with conversion slows to near zero. The range of ON variation is not large but has economic significance. For example, consider the benchmark

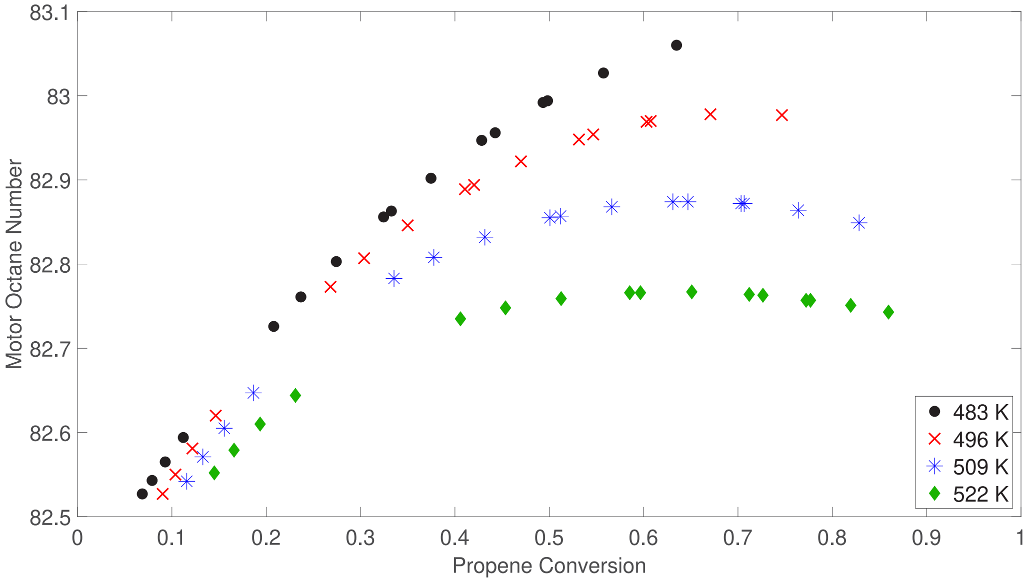

Figure 4. Motor octane number versus propylene conversion at various temperatures.

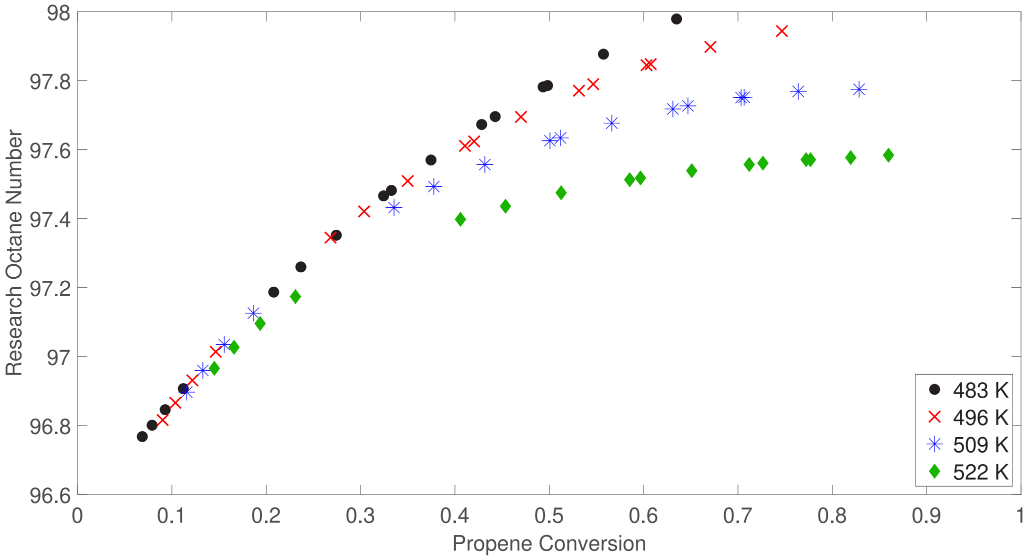

Figure 5. Research octane number versus propylene conversion at various temperatures.

NGL-to-liquid process given by Ridha et al.,[6] which uses catalytic dehydrogenation and oligomerization to produce 13 500 barrels day^{-1} of liquid hydrocarbon product, representative of an intermediate size NGL-to-liquid facility. An increase of one ON in the liquid product, about the difference observed between the low and high conversion cases here, valued at \$4 barrel^{-1} ON^{-1} (U.S. average value[8] in 2015) results in an increased product value of \$19.7 million year^{-1}. It should be noted, however, that ON is not the only important property that must be considered in evaluating a potential gasoline blend stock. In addition to the volatility constraint mentioned above, there are constraints on the olefin content of gasoline. Here, due to the specific microkinetic model used, the catalytic oligomerization product is an entirely olefin mixture, Even with the more complex model including paraffins, results indicate a low paraffin content in the product. The high olefin content may limit the amount of oligomerization product that can be used in the gasoline blending pool, suggesting that some hydrogenation of the product may be desirable.

The nonlinear relationship between ON and conversion can be partially explained by relating the average degree of branching (DOB) to conversion. Generally, a higher DOB correlates with a higher ON, consistent with the definition of ON. In this analysis, the degree of branching is given in terms of the average number of terminal carbon atoms per molecule in a mixture. Figure 6 illustrates that, at lower temperatures, the DOB increases almost linearly with respect to conversion. At higher temperatures, however, the DOB exhibits a nonlinear behavior and reaches a maximum with respect to conversion. Overall, the DOB trends well with both RON and MON.

The nonlinear relationship between ON and conversion is also explained through product distributions. Low conversion cases, a consequence of either low catalyst loading or high molar throughput, have approximately the same product mixture composition regardless of temperature. Figure 7 represents the fractional composition of a low conversion case with a space velocity of 9.2 mol$_{C_3}$ (mol$_{H^+}$)$^{-1}$ s^{-1}. The product is composed primarily of C_6 olefins that account for

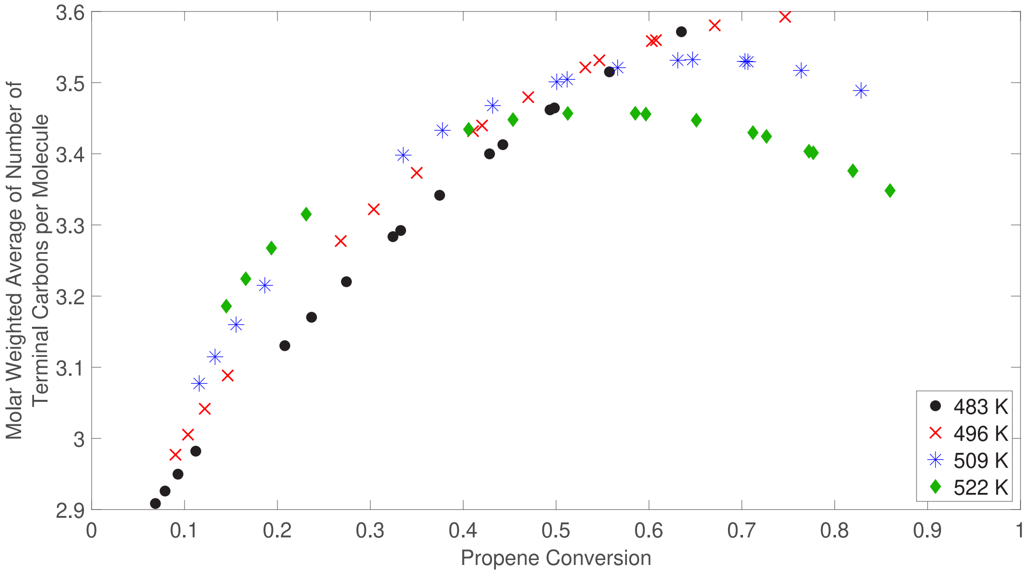

Figure 6. Degree of branching versus propylene conversion at various temperatures.

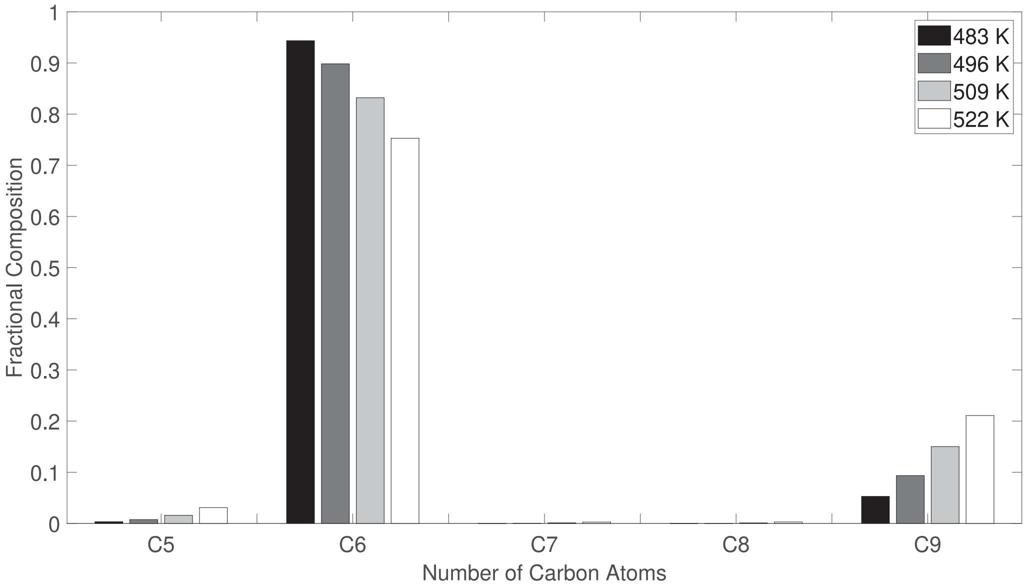

Figure 7. Fractional composition versus number of carbon atoms in a compound at various temperatures for the low conversion case. For this case, the space velocity is 9.2 mol_{C_3} $(\text{mol}_{H^+})^{-1}$ s^{-1}.

>70 vol % of the mixture. Higher conversion cases tend to vary more strongly in composition between temperatures. For example, in Figure 8, for a space velocity of 0.8 mol_{C_3} $(\text{mol}_{H^+})^{-1}$ s^{-1}, at 483 K, the product effluent contains primarily C_6 and C_9 compounds, with higher amounts of molecules with other numbers of carbon atoms, relative to the low conversion cases. At the same space velocity of 0.8 mol_{C_3} $(\text{mol}_{H^+})^{-1}$ s^{-1} and a temperature of 522 K, all the carbon numbers are well represented in the product mixture.

Despite the large number of effluent species considered by the microkinetic model, a relatively small group (9−12) of compounds dominated the effluent composition, constituting between 66 and 93 vol % of the effluent stream in all of the cases studied. Thus, a significant part of the results can be explained by the formation (or lack thereof) of the compounds in this small group. For instance, at low temperatures, the increase in ON with respect to conversion is largely explained by the increased formation of only two compounds with high pure-component ONs: 2,3,4-trimethyl-2-hexene and 3,4,5-trimethyl-3-hexene. Another example, at high temperatures, is that the decrease or leveling of ON with respect to conversion can be explained by the formation of 2-pentene, which has a low pure-component ON and represents nearly 20 vol % of the mixture. Reaction conditions drive different reaction pathways and hence the formation of different species; identifying compounds that have the highest impact (positive or negative) on ON enables catalyst designers to target specific reaction pathways that drive the formation of high ON product.

In order to identify favorable and unfavorable compounds with respect to mixture ON, a sensitivity analysis was employed using the product mixture of the high conversion case with a space velocity of 0.8 mol_{C_3} $(\text{mol}_{H^+})^{-1}$ s^{-1} as a basis. For this analysis, the molar flow rate of a compound in the product stream was increased by 50% and then decreased by

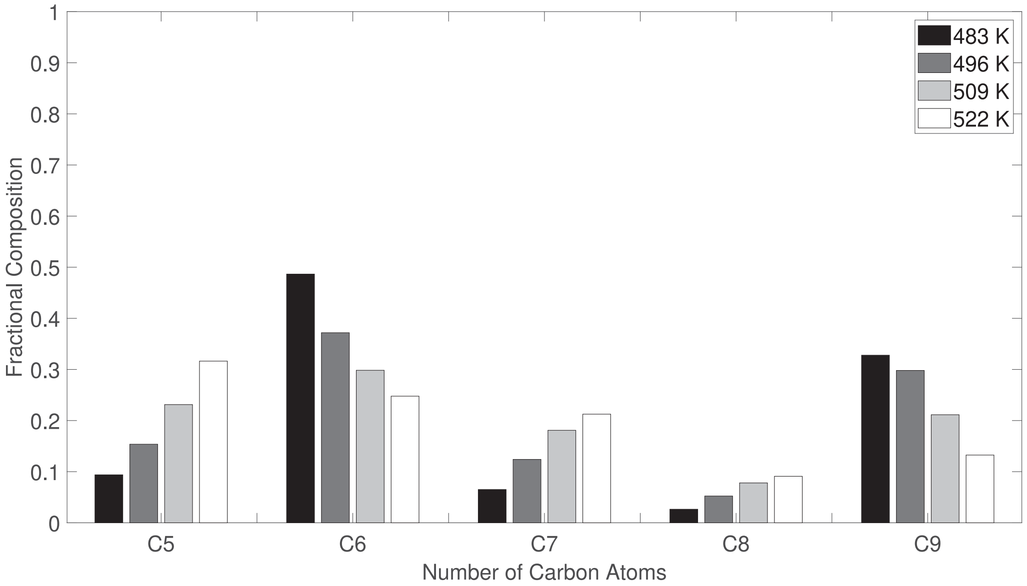

Figure 8. Fractional composition versus number of carbon atoms in a compound at various temperatures for the high conversion case. For this case, the space velocity is 0.8 mol_{C_3} $(\text{mol}_{H^+})^{-1}$ s^{-1}.

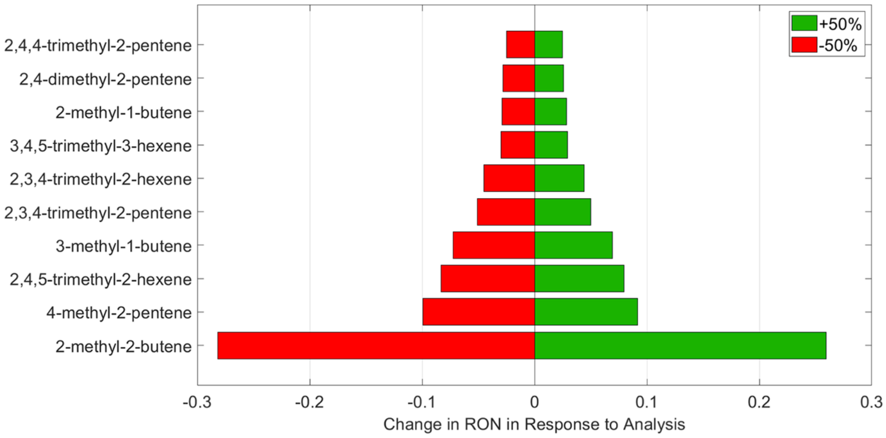

Figure 9. Ten most desirable components from the sensitivity analysis.

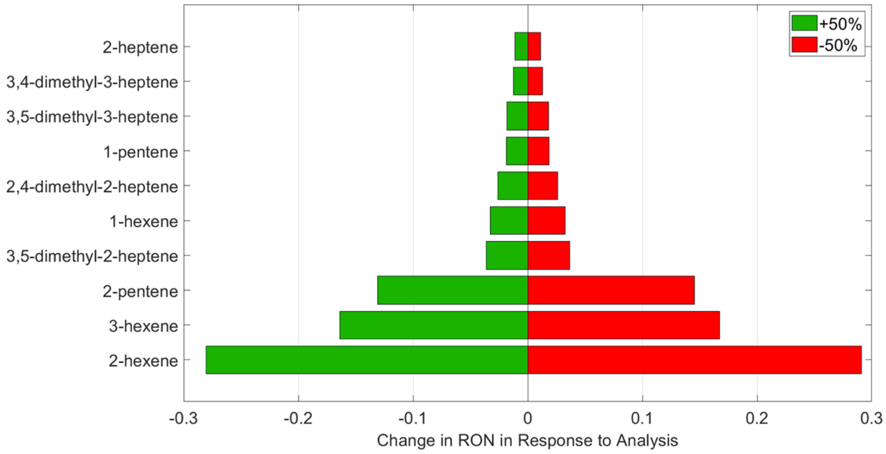

Figure 10. Ten most undesirable components from the sensitivity analysis.

50% while holding the molar flow rates of all other compounds in the product stream constant. For both the 50% increase and 50% decrease, the deviation of the mixture ON from its nominal value was determined. This process was repeated for each compound in the product mixture. A desirable compound will increase (and an undesirable compound will decrease) the product mixture ON when that compound's molar flow rate is increased. Figure 9 shows the 10 most desirable compounds and the response of the mixture ON to the sensitivity test. Figure 10 portrays the same for the 10 most undesirable products. For this example case, targeting the formation of 2-methyl-2-butene and avoiding the formation of linear olefins such as 2-hexene, 3-hexene, and 2-pentene will have the largest impact on maximizing mixture ON. This analysis serves to identify specific compounds to guide reaction pathways considered by catalyst and process designers.

4.2. Propylene and Ethylene Oligomerization. ON can also be calculated in response to varied oligomerization reactor feed compositions. In this second case study, two scenarios, one involving a pure ethylene feed and another involving a pure propylene feed, were considered. In both scenarios, the reactor temperature was 503 K, with a molar feed flow rate of 1.39×10^{-4} mol/s, and a constant molar conversion of 15.3%. Using the microkinetic model, the effluent composition was generated and the mixture ON calculated for each scenario. Table 5 conveys the RON and MON results for the two scenarios.

Table 5. RON and MON Data for Feed Composition Scenarios

feed type	RON	MON
100% propylene	97.0	82.6
100% ethylene	96.9	82.9

Between the pure ethylene and pure propylene feed scenarios, there was only a very small difference in RON and MON. The product distribution, however, was considerably different, as illustrated in Figure 11. When pure propylene was fed to the reactor, C_6 and C_9 compounds dominated the mixture. When pure ethylene was fed to the reactor, C_4 compounds were the most prevalent. In general, the microkinetic model results for oligomerization were multiples of the hydrocarbon feed molecule length. In this context, it should be noted again that the oligomerization reactor effluent is assumed to undergo a sharp vapor−liquid separation between C_4 and C_5 hydrocarbons, so the liquid product of interest does not contain any C_4 or lighter species. Thus, C_4 compounds do not contribute to the computed mixture ONs.

It is important to note that the liquid product molar flow rate, considering only C_5 compounds and heavier, is 6.81×10^{-7} mol/s for the pure propylene feed case and 1.59×10^{-7} mol/s for the pure ethylene feed case. Although the feed molar flow rates are identical, the liquid product molar flow rates are different by a factor of about 4.3, enough to alter practical process considerations beyond the comparison of ON. In this instance, the ON results are similar between the two feed compositions, meaning that the pure propylene feed with a higher conversion to liquid product may be preferred. More generally, other factors such as recycle rates or energy requirements should be considered in parallel with ON during the optimization of process design, deployment, and operation.

In a situation similar to the pure propylene case study in section 4.1, between 8 and 12 compounds constituted between 78 and 99 vol % of the liquid product mixture. In the pure propylene feed scenario, the liquid product mixture was dominated by C_6 compounds that generally have a lower MON and a higher RON. In the pure ethylene feed scenario, 2-pentene and 2-methyl-2-butene alone account for 65 vol % of the liquid product mixture. Together, these two compounds happen to have approximately the same pure-component ON as the C_6 compounds generated in the pure propylene feed scenario, resulting in a situation for which the results for RON and MON are practically the same for either feed scenario, despite their very different product compositions. However, since the calculation of RON and MON tends to depend on a relatively small number of dominant compounds in all of the cases studied, the product ON may vary significantly when comparing other types of scenarios. In this specific case, the ON provides guidance to catalyst and process designers that, for the given reaction conditions, there is little change in ON-based product value with regard to reactor feed composition.

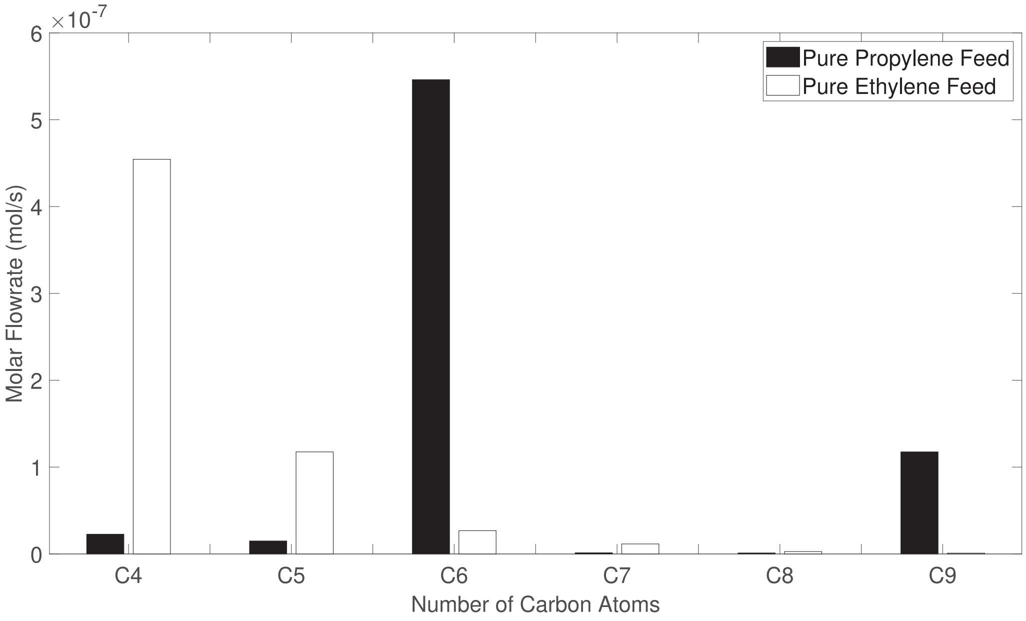

Figure 11. Molar flow rate per number of carbon atoms in a compound at various ethylene molar compositions for an ethylene or propylene feed mixture.

5. CONCLUDING REMARKS

A combined microkinetic and octane number (ON) modeling approach for evaluating an oligomerization reactor product stream was described here. This enables quantification of a mixture's economic value relative to other similar mixtures and guides process development toward higher-value products. Two case studies were used to demonstrate the use of the combined microkinetic and ON modeling approach. A case study on propylene oligomerization was used to show how the influence of reaction conditions on the product value could be studied. Results showed that ON generally increases with decreasing space velocity, increasing degree of branching, and increasing conversion. In an additional case study, for one specific set of reaction conditions and product separation configuration, results also showed that, though ethylene could be substituted for propylene as the feed with little change in the product ON, this would cause a significant reduction in product flow rate. It was also demonstrated in the case studies how a sensitivity analysis could be used to identify the most desirable and undesirable components in a mixture from the ON standpoint. It is expected that this information, together with case studies of the sort presented here, will provide guidance to catalyst and process designers as they optimize reaction pathways to obtain greater economic product value for NGL to liquid fuel conversion processes.

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Notes

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