Perspective

Molecular Engineering Approach in the Selection of Catalytic Strategies for Upgrading of Biofuels

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Introduction

Fuel is one of the archetypical commodities, which one rarely associates with precise molecular design. However, the ever increasing severity of environmental regulations on fuels have made refiners during the last decade embrace the concepts of molecular management and molecular engineering, which still keep elements of process design, but also aim at product design. The advent of different biofuels in the energy scene, particularly those from second- and third-generation technologies, produced from nonfood biomass resources, poses new challenges and research opportunities for fuel development and catalytic upgrading.[1]

The concept of *molecular management* has been implemented in refining operations for some time. In simple terms, molecular management implies having the right molecule in the right place, at the right time and at the right price.[2] By applying these concepts, refiners have developed separation and conversion processes that allow them to more accurately select the mix of crudes with properties that maximize the performance of products with higher demand at a given time (gasoline, kerosene, or diesel). The closely related concept of *molecular engineering* as applied to fuels implies a higher level of molecular manipulation, indicating a purposeful design of molecules with precise structures and well-defined properties. To achieve this high level of chemical specificity, the continuous improvement of catalytic materials is essential.[3]

A number of properties determine the quality of a given fuel. We can mention octane number, cetane number, sooting tendency, water solubility, freezing point, viscosity, flash point, cloud point, autoignition temperature, flammability limits, sulfur content, aromatic content, density, boiling temperature, vapor pressure, heat of vaporization, heating value, thermal and chemical stability, and storability. Many of these properties can be modified by catalytic upgrading. In designing a catalytic upgrading strategy, a refiner must know how each of these properties is affected by the structure of the molecule and how a given catalytic conversion of that structure in turn affects the properties.

For example, catalytic cracking on an acidic zeolite, converting long alkanes into shorter and branched hydrocarbons would increase octane number and vapor pressure, while decreasing viscosity and density. Of course, fuels have a large number of components and for many fuel properties the overall value for the mixture depends nonlinearly on the individual properties of the components.[4] However, it is certainly of great value to understand how the structure of a given molecule in the mixture affects each of the properties of interest. This knowledge can serve as a guide to determine what reaction paths would be the best candidates to optimize a specific fuel property of a complex mixture.

There are many examples in the literature in which the molecular engineering approach has been applied for the upgrading of fossil fuels. By contrast, the same rational approach has been used more sporadically in the upgrading of biofuels. The purpose of this contribution is to point out this opportunity to the chemical engineering research community.

Methodology

The notion of molecular engineering as applied to catalytic upgrading of fuels is illustrated in the conceptual triangle depicted in Figure 1. In order to optimize a fuel property of interest it is first necessary to develop a database of properties for the possible molecular components, which can either be obtained experimentally or predicted with reliable methods based on the molecular structure (*Relationship 1*). Then, one needs to obtain fundamental understanding on how different potential catalysts and processes modify the structure of a given reactant to obtain the resulting products (*Relationship 2*).

This understanding provides direction toward which specific chemical bonds will be broken or formed under specific

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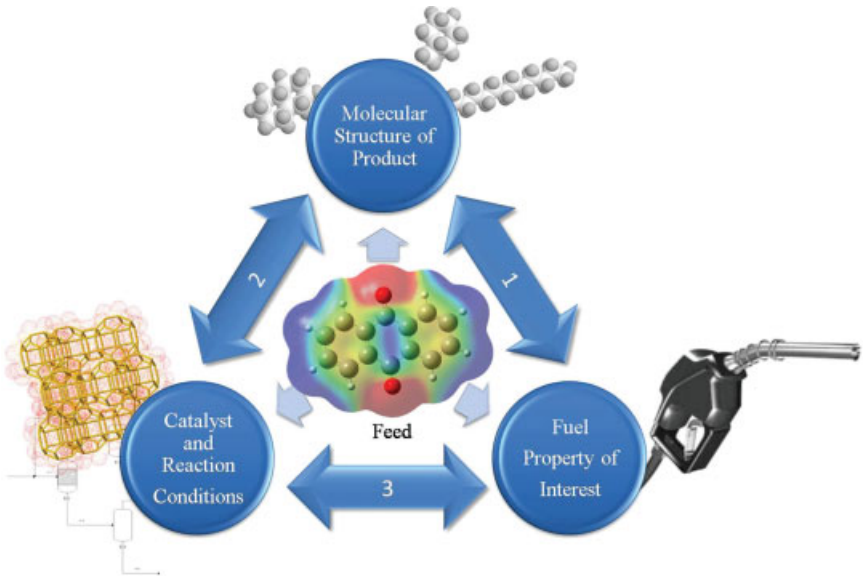


Figure 1. Conceptual overview of the molecular engineering strategy as applied to fuel upgrading.

conditions. We can identify the "12" path as the molecular engineering approach, while the direct path "3" would be an empirical approach. The rational approach takes into account that by knowing the relationship between molecular structure and the desirable fuel properties one has the ability to modify different aspects of the catalyst and the reaction conditions to optimize specific structures, resulting in the optimum properties.

Relationship 1: Molecular Structure-Properties

While it is advantageous to have reliable experimental data for each of the fuel properties of interest, in many cases the only information known about a given compound is its molecular structure. Therefore, correlations between fuel properties and molecular structure need to be used.

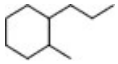
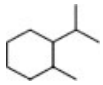
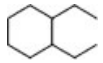
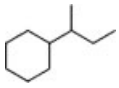
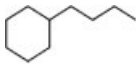
The most commonly used correlations are the so-called quantitative structure property relationships (QSPR), first used more than 40 years ago in agrochemistry,[5] but they have expanded onto many fields. QSPRs are models that correlate molecular descriptors, i.e., numerical values calculated from the molecular structure, to specific properties of the corresponding compounds. Molecular descriptors involve geometric, steric and electronic aspects of the molecule and can range from very simple physical parameters such as the number of carbon atoms or branches in a molecule, to more complex parameters such as dipole moment or surface area. Commercial QSPR softwares calculate hundreds of molecular descriptors. Specific, computationally expensive descriptors are sometimes needed and they can be calculated through higher order calculations such as density functional theory.[6] Ideally a researcher could use chemical intuition to select which descriptors are more relevant for a particular property. However, in many cases the relationships between molecular descriptors and properties of interest are too complex, so genetic algorithms and neural networks may be utilized to reduce the number of possible descriptors from several hundreds to a much smaller number that correlate best with the desired property.

After the descriptors have been selected, different models can be created through the use of linear regressions, nonlinear regressions, principal component analysis, genetic algorithms, and artificial neural networks. Care must be taken to ensure that the models capture desired trends without over-fitting the data. For this reason, cross-validation of the model is an important step. Application of QSPR to fuel properties has resulted in models that can estimate cetane number,[7,8] octane number (research octane number, RON, and motor octane number, MON),[9] and sooting tendencies[10] of any fuel component, only on the basis of the molecular structure.

Relationship 2: Catalyst-Reactivity-Structure

The understanding of these relationships at the molecular level has been the goal of many modern research studies in catalytic fuel upgrading. Elegant examples abound in the catalysis literature.[11] These relationships can be investigated following different approaches: in one of them, the effect of varying the reactant molecular structure is studied while keeping the type of catalyst unchanged. In another approach, the variable is the structure/composition of the material that catalyzes a fixed probe molecule. An interesting example of this type of studies has been the selective ring opening of naphthenic molecules on noble metal catalysts.[12,13] Only one endocyclic C-C bond per naphthene ring must be opened to preserve the reactant molecular weight while producing isoalkanes of high octane number. Over conventional hydrocracking catalysts, the yield of alkanes with the same number of C atoms as the cyclic reactant naphthenes is typically very low due to secondary cracking. Since 5-member rings open much more readily than 6-member rings, an acidic catalyst that catalyzes the ring-contraction reaction converting alkylcyclohexanes into alkylcyclopentanes coupled with a high-activity hydrogenolysis metal catalyst, such as Ir, was proposed.[12] This bifunctional catalyst is many times more selective for ring opening than conventional hydrocracking catalysts. Likewise, the alkane cracking reactions on FCC catalysts have been intensively investigated for many years; good correlations between

Table 1. Cetane Number and Micropyrolysis Index Values of Several Substituted Cyclohexanes, as well as a Linear Combination of the Properties Resulting from their Primary Products Once Reacted Over an Ir/Al_2O_3 Catalyst at 330°C and 500 psig of H_2

		FEED PROPERTIES		PRODUCT PROPERTIES	
1-ring naphthenic feed	Structure	CN	MPI	CN	MPI
1-propyl-2-methylcyclohexane		39.1	20.4	42.7	13.8
1-isopropyl-2-methylcyclohexane		30.8	22.5	28.3	14.9
1,2-diethylcyclohexane		39.0	20.4	36.5	13.8
sec-butylcyclohexane		35.3	20.4	36.1	14.0
n-butylcyclohexane		47.4	18.3	40.8	12.8

reactivity and chain length, as well as number and type of substituents have been found for different catalyst compositions and reaction conditions.[14]

The investigation of novel catalyst formulations has evolved from simple parallel screening of different catalysts to modern high-throughput techniques combined with theoretical calculations (DFT) that guide the selection of formulations, as opposed to empirical testing, and minimize the number of experiments. At the same time modern characterization techniques help to better understand the nature of the active site.[15]

Potential Applications in the Upgrading of Conventional Fuels

By putting together the two relationships (*Molecular Structure-Properties* and *Catalyst Reactivity-Structure)* it is possible to design catalysts and reaction conditions that produce the right molecular structure that maximizes the desired fuel property. For example, as shown in Table 1, from a database of experimental reactions on a given catalyst (in this case 1% Ir/Al_2O_3) and application of the QSPR method, we have obtained relative activities for the opening of the different C—C bonds in 1-ring napthenic molecules. This comparison was accomplished by measuring the primary product yields of 14 substituted cyclohexanes at low conversions in order to minimize secondary products. Yield ratios of products from C—C bond cleavage at various molecular positions were calculated which, when combined, result in the product distribution. Examples include the selectivity toward cleavage of the branch vs. the ring, the ring at substituted vs. unsubstituted positions, the branch at positions connected to the ring vs. not connected, and for 1,2 di-substituted cyclohexanes cleavage of the ring. The resulting products were then calculated to represent the product distribution.

From these relative reactivities one can predict the distribution of primary product for any 1-ring napthenic molecule, which in turn allowed us to calculate two important fuel properties for the product mixture, i.e., cetane number (CN) and sooting tendency, as measured by the micropyrolysis index (MPI). Conclusions of great practical importance have been obtained from this analysis. That is, while ring opening does not necessarily result in a significant increase in cetane number,[7] it does have a beneficial effect on fuel properties because it decreases the sooting tendency.[10] For example, the mixture of isoparaffins resulting from the ring opening of 1,2-diethylcyclohexane has in fact a lower cetane number (CN = 36.5) than that of the original feed (CN = 39). However, the sooting tendency decreases from 20.4 to 13.8 upon this conversion. Similar conclusion is found for all the 1-ring naphthenics investigated.

Potential Applications in the Upgrading of Biofuels

When one applies molecular engineering strategies toward biofuel upgrading, several important opportunities are presented. Each type of biofuel has inherently unique challenges associated with it. Many of these challenges arise from the presence of oxygen in the biofuel molecules. Oxygen can have some positive effects on fuel properties, such as lowering the vapor pressure, decreasing sooting tendency, and improving octane number. However, oxygen can also have a negative

impact on critical properties such as blending vapor pressure, storage stability, transport in pipelines, water solubility, corrosion, NO_x formation, toxicity, and heating value. Many of these challenges warrant the need for removal of oxygen from the system to make a more fungible fuel, which is compatible with the current infrastructure. Molecular engineering of biofuels is not the simple deoxygenation, but rather the controlled conversion of the oxygen functionality and how this conversion affects the fuel properties. Through this knowledge, catalysts and processes may be designed to only remove the specific oxygen atoms that pose the greatest problems in fuel applications, while minimizing yield loss and valuable hydrogen consumption. At the same time, the presence of oxygen can be utilized to take advantage of its functionality and condense small oxygenated molecules with low fuel value (e.g., propanal, acetic acid, furfural, etc.) into heavier hydrocarbon molecules, more appropriate for diesel or gasoline fuels, via organic reactions such as aldol condensation, ketonization, etherification, etc.

Estimation of biofuels properties

Estimation of properties, which are common for conventional fuels, may pose challenges when dealing with biofuels due to the impact of the oxygenated groups. For this reason, improved methods must be developed to predict fuel properties such as cetane number, octane number, sooting tendency, vapor pressure of biofuels and their blends with petroleum fuels.[8,16,17] Properties that are typically of minor concern in conventional fuels but have significance for biofuels include water solubility, thermal and chemical stability, corrosivity, and toxicity. Prediction of water solubility is very important, as this property has environmental, as well as refining and transport implications. Compounds soluble in water have a greater tendency to negatively impact the environment in lakes and drinking water. Water solubility also hinders storage and conventional pipeline transportation. Because of these inherent issues, the problem of estimating water solubility has been undertaken by a number of groups.[18] Correlations have even been obtained between water solubility and other fuel properties such as melting point, logP (i.e., log of the octanol/water partition coefficient ratio), and molecular weight.[19] Stability can be broken up into various subsets. Oxidative stability, for example, is a cause of concern for olefinic triglycerides and methyl esters. This can be estimated through the rancimat test (EN14212) or oxidative stability index (OSI).[20] Other forms of storage stability, however, are dependent on condensation and polymerization reactions between functional groups of neighboring molecules.[21] This is a difficult property to access for one compound alone, as it is highly dependent on the fuel matrix.

For example, in the case of pyrolysis oil, which contains many compounds, it would not be practical to evaluate and follow the variation of properties of individual compounds, but rather of all the molecules containing a given functional group. Model studies provide fundamental knowledge about the reactivity of specific functional groups on a given catalyst and the impact of the observed reactions on the targeted fuel properties.

In general, specific functional groups, such as aldehydes and carboxylic acids, which are known to react with each other, can be targeted and converted in order to improve the storage stability. Corrosivity, which is a major issue with pyrolisis oil, can be influenced by both metal content and pH of the fuel. Acidity measurements pH and pKa have been extensively predicted based on QSPR, group contribution, as well as spectroscopic techniques.[22] These types of models are essential for biofuels as many properties of biofuel molecules are unknown, and it may be very difficult to separate and measure them. As an example, fast pyrolysis oil contains over 400 different compounds.[23] Properties for many of these oxygenates have not been previously measured, although they all can have a significant impact on fuel properties.

Ideally, relationships are created such that not only one property, but a number of properties of interest are known for each potential reactant/product in a given reaction to measure the impact of a given conversion. This analysis is critical since it is not uncommon that some desirable properties are improved at the expense of others, as shown later. In most cases, an intermediate solution is reached in which all the target properties are in an acceptable range. An illustrative example can be seen in Figure 2 through the conversion of furfural over Cu or Pd catalysts. Furfural is typically derived from dehydration of sugars, but is also present in the product from the fast pyrolysis of biomass.[23] Due to the unstable nature of furfural (as of any other aldehyde), it must be converted to be used as a transportation fuel component. Therefore, the first step is to determine the properties of furfural and those of the potential products that could result from its conversion.

For example, the research octane number (RON) of each of the pure molecules was estimated through the use of a linear regression QSPR model by fitting data of 67 oxygenates and hydrocarbons to their molecular structure through the utilization of MDL QSAR software (version 2.2.0.0.446(SP1) from MDL Information Systems, Inc.). The result of this fitting is a model that can predict RON of any oxygenate species, based only on molecular structure. The RMS error of the dataset was 6.8, with a cross validation error (leave one out) of 8.9 RON. Likewise, vapor pressure for each compound has been estimated through the use of ACD/Labs Software V9.04 for Solaris. Water solubility was also estimated through a correlation with various other properties of the molecules.[19] These property prediction capabilities provide guidance on which reactions should be maximized in order to improve the fuel properties of interest.

For example, to illustrate the method, a comparison of changes in properties without considering the nonlinearities of the mixtures is made in Figure 2. Gas phase hydrogenation and decarbonylation of furfural were conducted over Pd and Cu at various temperatures in a tubular flow reactor. Properties of the feed and resulting products were estimated assuming linear mixing of the properties of the individual components.As furfural is converted over either Pd or Cu in the presence of H_2, properties of the compounds exiting the reactor are optimized under different conditions. If one wants to maximize the octane number alone, clearly Cu/SiO_2 is the better catalyst, operating at high conversions. On the other hand, if one considers the water solubility of the resulting fuel, Pd is the better catalyst as its products minimize increases in water

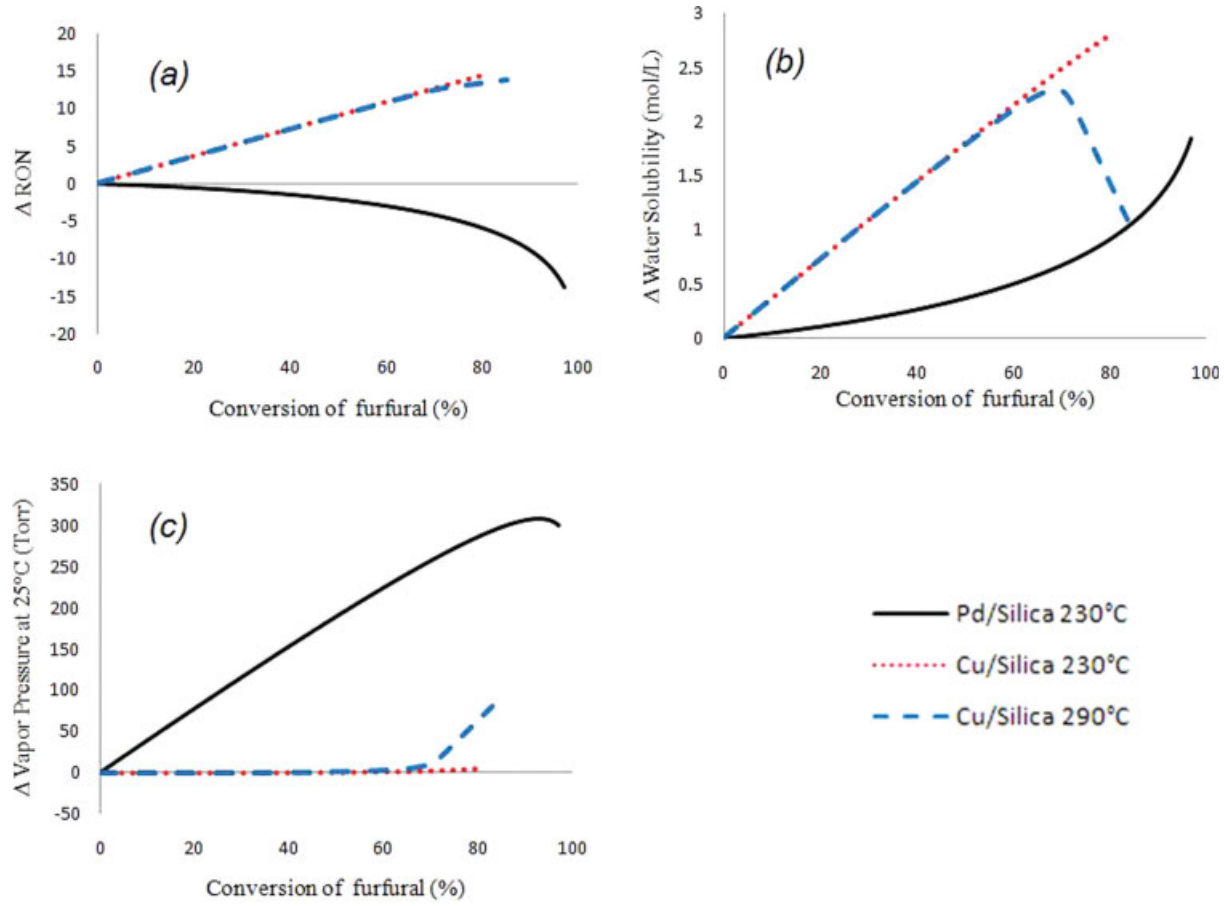


Figure 2. Change in (a) research octane number (RON), (b) water solubility, and (c) vapor pressure of products exiting a flow reactor across Cu or Pd catalysts as a function of feed conversion.

solubility. Copper also appears more promising in minimizing light compounds with high-vapor pressure as decarbonylation is avoided. Other properties, such as heating value, viscosity, and hydrogen consumption also play crucial roles in determining which catalysts or process condition should ultimately be utilized. This example illustrates that optimization of one property alone is usually not the best option. Property prediction combined with catalytic studies help optimize the process.

In this example, we have compared only two catalysts and two temperatures. Another dimension in the scheme of Figure 1 for the molecular engineering approach could be added by incorporating high-throughput catalyst design and testing and combinatorial analysis tools.[24] While a higher level of precision will need to consider the blending effects that may change the resulting properties by intermolecular interactions, analysis of the changes in properties of the individual components is a valuable first approach in defining catalytic strategies.

Refining of triglycerides

The most common process utilized today to upgrade triglycerides to fuels is based on the transesterification to methyl esters, or biodiesel. Both triglycerides and methyl esters still pose problems with stability and cold flow properties, making further upgrading attractive. Issues with triglycerides arise from four molecular aspects: long-chain lengths, olefin content, ester groups, and free fatty acids. The former two aspects can be improved through conventional processing well established in refinery operations, although selective hydrogenation of the olefin groups has been the focus of recent publications.[25] The latter two, however, lead to problems with water solubility, storage, and corrosion. Selective reaction of acid and ester groups has been the focus of many recent studies.[26] Over Pd catalysts, C=C double bonds are first hydrogenated to form saturated acids, followed by selective decarbonylation and decarboxylation of the oxygen species. Through this approach, some carbon is lost as CO, but at the same time less hydrogen is necessary in the process. This can be a very practical approach due to the large hydrocarbons involved. The loss of CO still results in linear hydrocarbon products well in the diesel range, with improved heating value, and once hydrogenated, the resulting products are linear paraffins, with a high CN. The main disadvantage of these paraffinic hydrocarbons is their poor cold flow properties.[27] In order to further improve the cold flow properties of the fuel, such as viscosity, cloud point, and pour point, the resulting deoxygenated hydrocarbons may be isomerized to produce branched isoparaffins. This process has been implemented commercially.[28] In this

commercial process, the vegetable oils are first hydrogenated and deoxygenated over conventional hydrotreating catalysts. The resulting n-paraffins then undergo mild isomerization over an acidic catalyst to produce isoparaffins with improved cold flow properties. While this process is very practical and utilizes existing equipment present in most refineries, the catalytic procedures themselves could potentially be optimized further. Sulfur species are inherently not present in vegetable oil while conventional hydrotreating catalysts are highly optimized to react to sulfur molecules and not oxygenates. Therefore, more active and selective metal catalysts, specific for oxygenates, such as those based on Pt and Pd, could be better fits for this application. Furthermore, one may fine tune the operating conditions to shift from hydrodeoxygenation to decarbonylation and decarboxylation which may also produce paraffins, or olefins in the absence of hydrogen or a metal with hydrogenation capability.[29] Future improvements could potentially be made where isomerization and hydrogenation are included in one reactor. This could potentially take advantage of the ability to isomerize linear olefins to branched hydrocarbons while hydrogenating in the same reactor. Ideally, one could maximize isoparaffin yield while minimizing hydrogen consumption and the number of reactors.

Refining of sugars

Biomass-derived sugars can be upgraded to conventional fuels through the application of molecular engineering strategies. Dumesic et al.[30] have been pioneers in this area and have applied molecular engineering concepts to formulate biomass refining strategies. Through the use of model sugar compounds, and knowledge of the fundamental reactions involved, they have proposed strategies toward producing valuable gasoline, diesel, and kerosene fuels from sugars by taking advantage of the oxygen functionality in the molecules. For example aiming at producing gasoline-type fuels from sugars, they have developed a PtRe/C catalyst capable of breaking both C—C and C—O bonds in sugar molecules, such as sorbitol and glucose. In a good example of utilizing the *Catalyst-Reactivity-Structure* relationship, Re was chosen as an additive to Pt due to the stronger bond strengths with O atoms that result when alloying these two metals,[31] and due to the higher deoxygenation rates exhibited by Re alloys.[32] In addition to removing active oxygen groups, the PtRe catalyst serves as a steam reforming catalyst, converting adsorbed CO and water to CO_2 and hydrogen, which is needed for further deoxygenation. This clever process also utilizes the exothermicity of the deoxygenation reactions to balance the endothermic reforming, which in turn provides H for removal of O via hydrogenolysis. The result is the production of monofunctional oxygenated hydrocarbons from sugars. As a second step, these additional functionalities can be upgraded by a variety of methods. Gasoline-range branched and aromatic hydrocarbons result via dehydration of the remaining oxygen groups followed by acid-catalyzed cyclization over HZSM5. Alternative methods were proposed to produce linear light diesel-range molecules through aldol condensation of active ketones and aldehydes. This condensation was accomplished in two methods. The first one was elimination of carboxylic acids via titration or ketonization followed by basemetal catalyzed aldol condensation and hydrogenation over $CuMg_{10}Al_7O_x$. The second one was aldol condensation hydrogenation over $Pd/CeZrO_x$, with no additional pretreatment.

They have also proposed the acid-catalyzed dehydration of sugars to furfural compounds,[33] which can be further reacted with small ketones, produced either by the aforementioned reaction over PtRe or by reaction with acetone produced through glucose fermentation. With base-catalyzed aldol condensation, larger hydrocarbons are produced which can subsequently undergo dehydration and deoxygenation to form large diesel range paraffins.

None of these elegant strategies for producing fungible fuels from nonfungible molecules would have been possible without fundamental knowledge of the individual catalytic reactions. Although the reaction conditions and catalytic functionalities are not completely optimized, these studies provide excellent direction for future research. The concepts are based on molecular understanding of not only the desired molecular structure with desired fuel properties, but also the relationships between specific functional groups and the nature of the catalyst.

Refining of bio-oil

Production of bio-oil by fast pyrolysis is a very interesting area for fuel upgrading. Bio-oil inherently contains several hundreds of different species which must be upgraded in order to produce a fungible fuel. The relatively low operation and capital costs of bio-oil compared to other biofuels make it attractive.[34] However, the poor inherent properties of this biofuel lower its potential for widespread application. The types of compounds present in bio-oil range from light to heavy oxygenates with a large variety of functional groups. Bio-oil cannot be separated via traditional distillation as many of its components polymerize upon heating, resulting in the formation of solids. On the light end, small acid compounds such as acetic and propanoic acid pose corrosion problems. Because of this, pretreatment steps to remove the most active functional groups are required before any traditional upgrading can be achieved.[35] While conversion studies have been conducted using bulk bio-oil over either traditional hydrotreating catalysts or acidic zeolites, this is likely not the best approach. Ideally, a process which condenses the light ($<$C5) acids, aldehydes, and ketones into higher molecular weight hydrocarbons would be desirable. Removing reactive groups of the larger aromatic oxygenates, and, thus, inhibiting oligomerization to low-value solids and improving the fuel stability would be highly desirable. The conditions required to achieve these results are vastly different. Acid-catalyzed ketonization and aldol reactions would be required for the condensation of small oxygenates. By contrast, metal catalyzed mild hydrodeoxygenation would be required for the heavier compounds.

Upon simple addition of water, bio-oil has been shown to separate into an aqueous phase containing carbohydrate derived compounds, while heavy lignin derived compounds settle to the bottom.[36] Through the use of this, as well as known interactions between model compounds in the two phases, an optimized approach for creating fungible fuels from bio-oil could potentially be developed, similarly to the upgrading of sugars. Knowledge derived from the use of model compounds in fundamental studies will be essential. In fact, many model compound studies that might be almost

directly applied in the bio-oil upgrading have actually been studied in the development of specialty chemicals, fine chemicals, and pharmaceutical products.[37] Small acids and aldehydes are present in bio-oil, and their selective condensation to form higher value products by producing larger hydrocarbons connected through C—C bonds could be very desirable. C—C linkages are preferred in fuels over C—O linkages such as those in ethers or esters, as C—C condensed products can undergo further hydrotreatment while maintaining their molecular backbone. Model compound studies for the production of pesticides, pharmaceuticals, or solvents have been conducted toward producing ketones by acid-acid, acid-aldehyde, aldehyde- aldehyde, or aldehyde-ketone condensation to form C—C linkages via aldol condensation over either solid acidic or solid basic catalysts.[38,39]

At the other end of the spectrum, heavy lignin-derived species present in bio-oil exhibit stability issues as they are prone to oligomerization, and can result in heavy compounds that solidify easily and have low fuel value. For this reason, it is desirable to have an alternative strategy for the heavy oil-soluble compounds present in bio-oil. A possible strategy to upgrade these compounds is mild hydrogenation and deoxygenation of the most unstable functional groups. These types of model studies have received moderate attention in recent years. For these types of reactions, it is desirable to selectively hydrogenate the oxygen functionalities, while avoiding wasting valuable hydrogen in saturating aromatic rings. Model aromatic compounds, such as guaiacols, present in bio-oil have been reacted over commercial hydrotreating catalysts with decarbonylation and decarboxylation functions that remove the oxygen groups.[40] Not much work has been done, however, using more novel metal catalysts with improved selectivities.

Conclusions

In summary, biofuels upgrading offers new challenges to researchers, but a great potential economic impact for novel catalysts and processes. Maximum benefit will be obtained from these developments if the rational approach of molecular engineering is employed. In this approach, it is necessary to know how the target fuel properties of interest are affected by the molecular structure of the product, which in turn results from the interaction of the feed and the catalyst under specific process conditions. A detailed fundamental knowledge of these relationships will make the development of biorefining processes much more effective than if empirical approaches are employed.

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