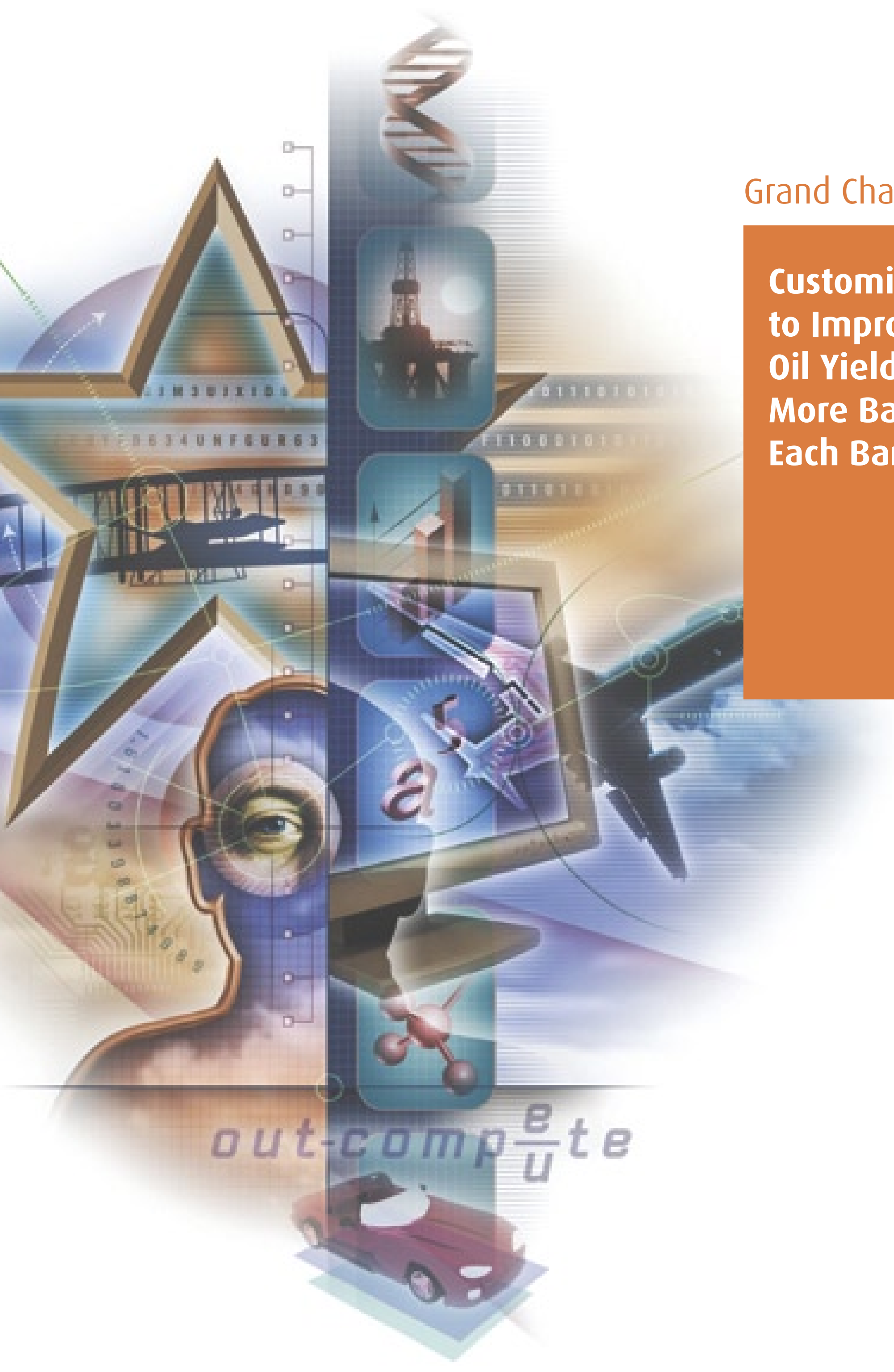
High Performance Computing and Competitiveness



Grand Challenge Case Study

Customized Catalysts to Improve Crude Oil Yields: Getting More Bang from Each Barrel

Council on Competitiveness

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In its natural from-the-Earth form, known as "crude", oil is sent to refineries where it is processed into a range of products with differing economic values. However, today's processing does not account adequately for the fact that crude oil's chemical composition varies substantially depending on the oilfield from which it is extracted. Differing crude oils need to be matched with specially designed catalysts during the refining process in order to increase and refine the output of higher-valued products. Successfully developing these specialized classes of catalysts requires an increased understanding of complex surface reactions at the molecular level. This can be achieved only by extending the reach and precision of experimental methods in concert with insight from computational models of the catalysis process. Such models would be so complex that they would require high performance computers with petaflop capability to run them within a reasonable amount of time. If this can be achieved, the payoff would be dramatically increased yield of high-value products from high- and low-quality crude oil, reduced environmental contamination, and progress in the development of energy alternatives such as synthetic fuels.

Variations in Crude Oil and Refining Processes Affect Product Output

Crude oil is extracted from underground or undersea reservoirs as a complex mixture of organic liquids. It varies in color and composition from one oilfield to the next, ranging from pale yellow thin liquids to heavy black viscous matter. In its natural state, this mixture is of little use and, therefore, of limited economic value.[1, 2]

It is the refining process that converts these mixtures into an array of useful products—gasoline of various grades, jet fuel, diesel fuel, lubricating oils, waxes, petrochemicals, pipeline quality natural gas, asphalt, and other items. Different oil mixtures can be refined more or less successfully into different products, some of which have a much higher value than others. Getting more of the higher-valued products from a given quantity of crude oil increases its net economic value.[1]

During the course of the twentieth century, demand has grown for higher-quality fuels, measured both by energy efficiency and minimization of waste ("clean" fuels). In response, the oil industry has developed refinery processes to increase its ability to produce higher yields of quality fuels, such as high-octane gasoline, and to isolate and produce additional products critical to competing in the global market. One of the most important of these refining processes is "catalytic cracking." In this process, oil molecules are broken down into different, more useful molecules through the application of a "catalyst", or substance that promotes a chemical reaction without itself being chemically changed or consumed.

"Cracking" the Cracking Process

The objective of catalytic cracking is to maximize the yield and variety of fuels that can be obtained from crude oil. During the refining process, different chemical catalysts are mixed with the crude oil in order to break down ("crack") the oil molecules, resulting in new molecules. Some catalytic processes occur in the presence of hydrogen ("hydro-cracking") and oxygen, while others exclude these elements. Regardless of the catalyst used, the ultimate objective remains the same: Create better, more useful molecules, which may be in the final form needed (i.e., the final product) or may be agents to create the final product desired. Catalytic processes also can eliminate harmful molecules or change them to harmless molecules.

The cracking process in a refinery is similar in concept to the way the body processes food. The body uses chemicals and proteins (catalysts) to break down ("crack") food into a form that the body can use effectively. For example, carbohydrates are "cracked" into sugars for energy. A catalytic converter in a car also performs a "cracking" process. In a car, the fuel components that are not burned must be expelled as exhaust. The catalytic converter uses a catalyst to break down the carbon and other chemical molecules in the exhaust into different chemical molecules. In this case, the result is molecules that are less noxious to the environment. (See Table 1.)

Early natural catalysts were clay. Later, synthetic catalysts in both powdered and highly porous solid forms were developed with much higher internal and external surface areas. Larger surface areas are critical. The more simultaneous

Body	USES	proteins	TO BREAK DOWN/CONVERT	carbohydrates	INTO	sugar
Catalytic converter	USES	catalyst	TO BREAK DOWN/CONVERT	carbon molecules in exhaust	INTO	chemical molecules less harmful to environment
Refinery	USES	catalyst	TO BREAK DOWN/CRACK	crude	INTO	gasoline, heating oil, etc.

Table 1

contact between the surface of the catalyst and the crude oil molecules, the faster the catalysis (chemical reaction) occurs, changing the crude oil into something different.[3, 4]

The way that a catalyst interacts with the crude oil on a molecular level determines what the end product will be, as well as how fast that conversion will happen. Which catalysts are used depends on the grade of the crude oil as well as the desired end product (heating fuel, gas for cars, fuel for jets, etc). For example, if jet fuel is needed, a certain catalyst is used to convert crude oil molecules appropriately to achieve this end product. If another fuel or petroleum compound is needed, a separate catalyst may be required to create a different output through the reaction process. The more specialized the fuel and the more specific the chemical characteristics desired of that fuel, the more specialized the catalyst must be.

New Catalysts Needed to Advance Product Development

As important as catalysts are to the refining process, they have not changed much in recent years. A few classes of catalysts serve as the workhorses across the whole range of crude oils. This means that variations in crude oil are not being matched closely by corresponding variations in the catalysts that are used. This failure to match catalysts closely to crude oil by its composition means that less of the higher-quality product is obtained, and the resulting yield pattern is inefficient.[2] So-called "designer" catalysts are needed that will selectively interact with the crude oil molecules, similar to pharmaceuticals that are designed to selectively act on "bad" cholesterol without harming "good" cholesterol.[4] Such catalysts would enable the oil and gas industry to dramatically increase the variety and yield of precisely targeted, high-value products from varying grades of crude oil.

An oil company executive articulated the dilemma: "Today it's not really practical to attempt to design things precisely, that is, to change the catalyst depending on what is coming in (the type of crude oil feedstock). The time to design and test a catalyst is prohibitive, so you use classes of catalysts. If you could customize the catalyst for each one of the types of crude oil, chemists say you could increase the yields substantially."[2]

Grand Challenge: Accelerate the Development of "Designer" Catalysts by Computationally Modeling Surface Chemistry Reactions with Nanoscale Precision

The oil and gas industry faces an enormous challenge that is essentially intractable: *Create feasible computational models with nanoscale precision of the surface chemistry reactions of prospective catalytic agents with each crude oil variation.* Such models are essential for increasing the understanding of the catalysis process in order to create customized catalysts. Because these models will be so complex, dramatically more powerful high performance computers with petaflop capability will be required to run them within a reasonable amount of time.

During the last 5-10 years, computational surface science and catalysis has emerged as an important collaborative partner to experimentation, which provides the critical data needed to create a significantly improved understanding of these complex phenomena.[6] Both must be pursued in tandem. However, an oil industry executive explained current computational limitations this way:

> "The ability to actually do computational chemistry on surfaces—interactions between a mineral surface and a fluid like oil or gas, or reactive surfaces when you design catalysts for processing—that's a problem that simply is not doable today at the level of precision required. It's a matter of being able to model and understand surfaces in a much finer structure. These catalysts are really nanostructures. You want to see what happens when you impinge other molecules on them—how efficient is

the reaction. Well, in the real world, the surface is for all practical purposes almost infinite compared to the molecules that are reacting."[2]

A renowned catalysis expert further explained, "We have reached the limits of experimental and theoretical surface chemistry. Developing the next generation of catalysts requires theoretically precise computational models, coupled with more compute capability, to be able to describe interactions at a precision of 2-10 nanometers."[4] At that level, the surface chemical interactions of single molecules could be observed. (See Figure 1.)

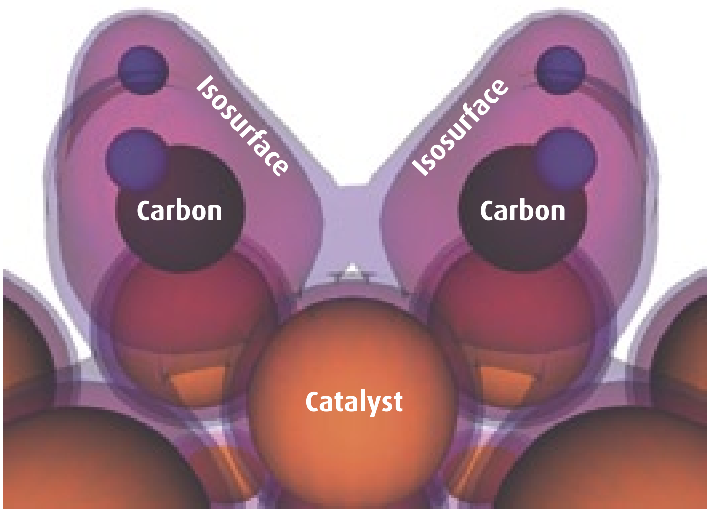

Figure 1 A computational model of the critical point (i.e. "transition state") where the carbon-carbon bond of ethylene has been "cracked" (broken). The absorbed molecule of ethylene is enclosed by two electron density isosurfaces.

The detailed understanding of transition states is key to determining how quickly a reaction will occur on a given catalyst. However, because the transition process occurs so rapidly (in femtoseconds/quadrillionths of a second), the details can not be viewed experimentally. Computational methods represent the only means to study them.

Image Courtesy L. Grabow, M. Mavrikakis, University of Wisconsin – Madison

Computational models must account for the fact that there are millions of these individual molecules in any region of observation during the reaction process. An analogy to the complexity of modeling and simulating the precise movements of millions of molecules might be likened to the process of distinguishing a winner in a closely contested Olympic race. While it may appear that two or more runners are crossing the finish line at the same time, advanced measuring devices differentiate each runner's performance time to the hundredth of a second so that a winner can be determined precisely. Now imagine the difficulty in distinguishing and measuring millions of runners crossing the finish line together in a pack. Devices might be required to measure performance to the billionth (nano) or trillionth (pico) of a second.

This is similar to the complexity of precisely accounting for the movements and interactions of millions of molecules, and is why petaflop (quadrillion operations per second) computational performance is essential. Algorithms and calculations also must be developed that reflect the changes that result as these millions of molecules collide and either bind to or bounce off of each other. These surface chemistry reactions (i.e., the interaction of these millions of molecules) must be measured on shorter and shorter time scales in order to distinguish and understand the effect of each of these "events", or molecular movements that must be modeled in the simulation. These time scales must move from today's milliseconds and microseconds to "nanoseconds to picoseconds and even to femtoseconds."[5] Just moving from milliseconds to nanoseconds is a millionfold increase in events, reinforcing the need for petaflop computing capability.

Adding to the computational complexity is the fact that catalysts change their surface structure (though not their molecular structure) in the presence of the molecules they are trying to chemically change (in this case crude oil molecules). The surface structure of a single catalyst is so flexible that it can morph like an amoeba into any number of different formations, depending on the kind of crude oil with which it is interacting. This is the wonder of the catalytic process, but also another factor that must be considered in the computational models. Algorithms and calculations must also consider aspects of the chemical bonding processes across the periodic table.[4]

The complexity of the computational models and the need for greater compute capability also changes depending on the molecular structure of the catalyst being studied. For example, a recent computational study of surface chemistry reactions involving just a small number of hydrocarbon molecules required three days of run time to completion on a 1000 processor IBM SP high performance computing system. Now consider the computational requirements if the carbon atom is exchanged for a platinum atom, an important catalytic material with high potential for the production of efficient fuel products. Taking into account that a minimum of 27 platinum atoms are needed to model the catalyst's surface, a minimum of 125 times the number

Petaflop computational performance is essential.

of computations mentioned above would be required, and it would take close to a year to run the model on the same high performance computing system. Since models must be run many times in order to make even modest progress in the discovery process, realistic turnaround time should be several hours instead of years, months, or even days. Running this model in hours requires a petaflop-capable system.[6]

It is also important to note that the models must represent the catalysis process within a contained environment because the real-world process occurs within a physical refinery. For example, suppose a catalyst, which might work well in accelerating a desired reaction, also happens to be highly corrosive in other environments? While it might produce the desired product, the process could be damaging to the refinery and require a re-design of the containers. The models must help scientists and engineers to understand not only what is chemically possible, but also what is economically sustainable and feasible within the boundaries of the refinery.

Economic and Competitiveness Benefits

By increasing the understanding of surface chemistry interactions of crude oil and potential catalytic agents at the nanoscale level, selective "designer" catalysts can be developed to help the oil and gas industry reduce costs and enhance profitability. For example, British Petroleum announced that the use of a new catalyst in one refining process was expected to result in direct savings of at least 10 percent, and potentially up to 80 percent of associated production costs.[7]

Using such customized catalysts, instead of catalysts from a limited number of classes developed to fit average conditions, has the potential to increase the yield from lower grades as well as from higher-quality crude oil. Every sector of the economy is dependent in some way on the volume, quality, and/or variety of these yields. Each day, the United States consumes more than 840 billion gallons (20 billion barrels) of refined petroleum.[8] Improving crude oil yields by even a few percent could have a ripple effect on multiple segments of the economy, as well as potentially generate millions of dollars of additional revenue for the oil and gas industry. As "designer" catalysts turn a larger percentage of a given quantity of crude oil into higher-valued products, they may do it without the need for extensive modifications to processes or an increase in capital investment. Oil companies could achieve higher productivity by effectively increasing their recovery rates and could greatly increase their return on investment in oil refining.

If appropriate catalysts can be developed, "designer" fuels and side products can be created that match certain market needs, such as materials with unique properties. Customers would have available a larger supply of the types of products they most demand, as well as new, customized products currently not available.

Selective catalysts also are critical for meeting the growing number of environmental regulatory requirements. Catalysts already have played an important role in helping refineries meet environmental standards, in the development of fuels free of sulfur and nitrogen components, as well as in the creation of replacements for the chlorofluorocarbons that are harmful to the ozone.[7] But more can be done. For example, low-grade crude oil contains a higher percentage of sludge and other waste products. Specialized catalysts could help convert more of that waste into useable products while simultaneously reducing the environmental impact on air, water, and soil as waste byproducts are reduced. And as waste byproducts are reduced, society will move a step closer to the realization of a green economy.

More precise understanding of advanced catalytic reactions is not only key to the efficient and clean production of petroleum products, it is on the critical path to advancing development of energy alternatives.[9] The pace of fuel cell development, for example, is highly dependent on higher precision computational modeling of catalytic reactions. Experimental techniques cannot provide sufficient detail to understand the complexity of these systems.[7] Catalysts are also critical to the development of synthetic fuels. If the price of crude oil continues to rise, the need for new, economic synthetic fuels will become more important.

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The Council on Competitiveness is a nonprofit, 501(c)(3) organization as recognized by the U.S. Internal Revenue Service. The Council's activities are funded by contributitions from its members, foundations, and project contributions.

Design: Soulellis Studio

Cover Illustration: Tom White, tomwhite.images-illustration & design

This work was supported by the U.S. Department of Energy, under grant DE-FG26-04NT42101.

Printed in the United States of America

Council on Competitiveness
1500 K Street, NW Suite 850 Washington DC 20005 www.compete.org