Research aims for cleaner crude from Canadian tar sands

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Demand for gasoline and other automotive fuels in emerging markets is expected to be met by growth in oil production from North America. Proven Canadian oil reserves are the third largest in the world, and the majority of those deposits are tar sands in Alberta. Tar sands contain a heavy oil, called bitumen, that is found mixed with clay and water.

The viscosity and chemical composition of bitumen makes it difficult to extract, transport, and refine. Technological improvements have made its production economically feasible, though this comes at an environmental cost. In US refineries, processing crude from the oil sands produces more greenhouse gases than the typical crude.

Researchers and companies are working to reduce the environmental impact of bitumen production by engineering new catalysts to efficiently clean the dirty crude. They are also working to convert waste from bitumen refining into materials for renewable energy.

Light crude oil from countries in the Middle East flows freely at room temperature because it mainly contains short hydrocarbons that are easily converted to fuel. Bitumen, in contrast, is a mixture of long hydrocarbons and large aromatics that creates a material resembling cold molasses. Producers can recover this crude by directly mining it. In deeper formations, they inject hot steam into tar sands, melting the bitumen so it can be pumped to the surface.

Generating the steam involves burning natural gas to boil water, which is one source of emissions during bitumen production. Canadian oil companies are looking for new extraction methods that use less steam. Suncor, based in Alberta, and Imperial Oil, based in Calgary, are pilot testing methods of bitumen recovery by injecting solvents such as propane or butane instead of steam. Less heat is needed inside the reservoir because the solvents also thin the bitumen. Separating and recovering the solvents at the surface are keys to the economic viability of the process.

Another energy-intensive step of bitumen production is processing, or upgrading, the crude once it reaches the surface. The goal of this step is to generate a material suitable for further refining into lighter fuel hydrocarbons.

Some bitumen is upgraded by dilution with lighter oil or natural gas condensate, reducing the viscosity of the crude so it can flow through pipes to a refinery. Another form of upgrading occurs in the field. The crude is treated with heat, hydrogen, and supported metal catalysts to chemically alter the heaviest fraction of bitumen. The goal of field upgrading with catalysts is to crack long hydrocarbons into small components; remove contaminants like sulfur, nitrogen, and heavy metals; and produce a material similar to diluted bitumen.

Typical upgrading catalysts are made from cobalt, nickel, and molybdenum. Several properties of bitumen can reduce the lifetime of the catalysts. The large molecules in bitumen clog pores, leading to active sites inside the catalyst, and side reactions during hydrogenation can smother the surface with a thin layer of carbonaceous coke.

To make these upgrading catalysts more efficient, some researchers are swapping supported catalysts for particles made from similar metals. These particles do not contain cloggable pores, and their submicron dimensions make the active sites easily available to the components in the crude.

At The University of Texas at El Paso, Russell Chianelli and colleagues have upgraded Canadian bitumen with molybdenum disulfide particles and hydrogen gas at ambient pressure, rather than high pressures usually needed for this process. The bitumen and particles are mixed in a reactor heated to more than 400°C. The metal particles pluck hydrogen from the aromatic cores of asphaltene contaminants. This generates free radicals that cleave saturated hydrocarbon chains from the asphaltenes. Then the catalysts redistribute the hydrogen from the aromatic cores to the hydrocarbon chains, creating lighter fuel molecules that evaporate from the reactor and condense in a collection vessel. The dehydrogenated cores remain in the reactor in the form of a solid cake containing heavy metal contaminants and catalytic particles.

Researchers in the Catalysis for Bitumen Upgrading and Hydrogen Production Research Team at the University of Calgary, directed by Pedro Pereira-Almao, think nanoparticles could be used to bring cleaner crude to the surface, eliminating the need for further upgrading.

The research team dissolves hydrogen and suspends nanoparticle catalysts in a heavy fraction of crude bitumen and injects the mixture into a simulated tar sand. The catalysts crack the longer hydrocarbons, hydrogenate some aromatic components of the crude, and remove some of the sulfur contaminants. "It's a one pot reaction that does everything: produce the oil, reduce its viscosity, and send it to a refinery," said

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Carlos Scott of Pereira's group.

The nanoparticles remain in the reservoir as the oil is produced, so once a reservoir contains the catalysts, new particles may not need to be added frequently. Under laboratory conditions, the *in situ* catalysts remain active for three to five months, and they do not plug pores in the reservoir, Scott said.

If the process works in the field, Scott said it could improve the energy efficiency of bitumen production by only requiring one energy input to produce and upgrade the oil, rather than a burst of heat to produce the oil and more energy to upgrade it.

In situ bitumen recovery at the Surmont oil sands project in northern Alberta. Credit: ConocoPhillips (November 2014).

As research continues to find ways to improve the environmental impacts of tar sands production, changing economic conditions could impact development. Falling oil prices threaten to curb future tar sands development, as well as stall plans to construct a pipeline to carry crude from Alberta to US refineries, which received the majority of Canadian oil exports in 2013.

Though it is unknown how long oil prices will remain low, one Canadian money manager thinks that energy economics over the next few decades will continue to disfavor the tar sands as a source of fuel. Leo de Bever, soon to retire as CEO of the Alberta pension fund AIMco, envisions a different use for the roughly 170 billion barrels of crude bitumen reserves: petrochemical feedstocks for plastics.

Researchers are also considering ways to use waste from bitumen refining in clean energy applications. Bitumen refining waste contains a collection of compounds called asphaltenes, which contain polyaromatic rings dotted with heteroatoms like oxygen, nitrogen, and sulfur. These gooey compounds are typically removed from crude oil and used as tar for roads and roofs.

James Tour and his colleagues at Rice University have converted asphalt into a porous material for capturing carbon dioxide at natural gas wells. Asphaltenes also absorb light and conduct charge, thus acting as an organic semiconductor. Chianelli, Manuel Ramos, and colleagues are exploring their use as sensitizers in solar cells.

Other North American crude oil reserves can be found in the United States and Mexico as deposits of heavy oil. This crude is less viscous than bitumen, but it is still thick enough to require similarly energy-intensive processes for extraction and upgrading. Chevron has been producing heavy oil from the Kern River field in California for more than 50 years. Cesar Ovalles, Technical Team Leader of Global Project Support in the Petroleum & Material Characterization Unit at Chevron, says the heavy oil research involves finding ways to efficiently clean the dirty crude.

Like bitumen production, improving the energy efficiency of heavy oil extraction involves research to extend the lifetime and reliability of upgrading catalysts, as well as reducing the catalysts' consumption of hydrogen gas, he said. Ovalles is working to characterize the composition of heavy oil to enable researchers to improve the efficiency of distilling the crude.

North American oil reserves present an opportunity for fuel production. Only about 15% of Alberta's established crude bitumen reserves are under active development. Heavy oil in formations underneath Utah, Colorado, and Wyoming is not in commercial production yet. Mexico has recently reformed its constitution to end the state-owned monopoly on the country's oil development.

Should these reserves go into commercial production, research in laboratories and pilot projects throughout the region could help new plants efficiently convert the dirty crude into cleaner fuel. □

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