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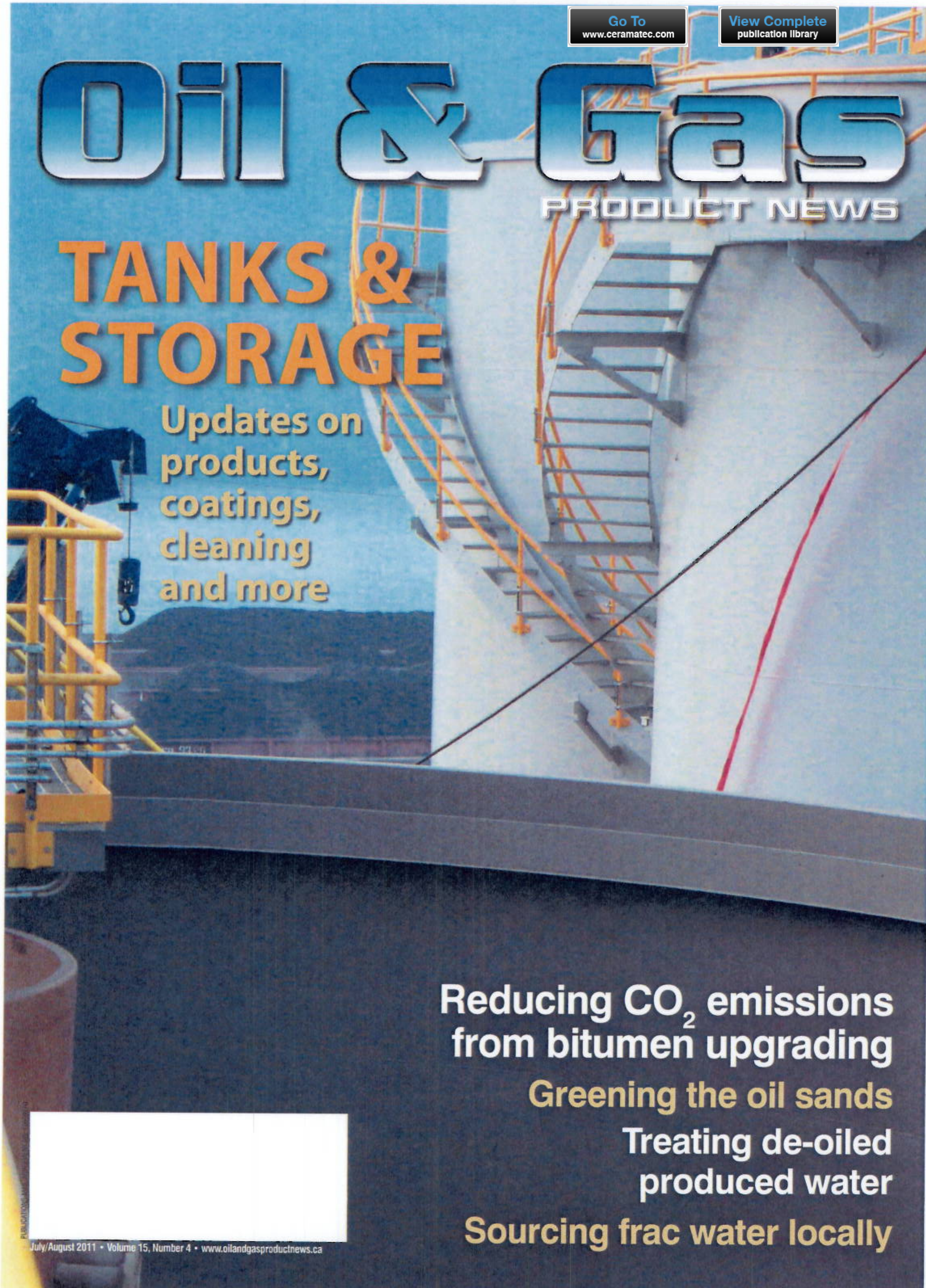

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Reducing CO_2 emission from bitumen upgrading

by John Gordon

The CO_2 emitted from production of oil derived from oil sands is of concern to many groups focused on global warming. With partial funding from the U.S. Department of Energy, researchers at Ceramatec Inc. have been developing technology expected to provide a path that will significantly reduce the amount of CO_2 emitted during the upgrading of feedstocks bearing heteroatoms such as sulphur, nitrogen and which contain heavy metals.

The team has experimented with kerogen derived oil (shale oil) and heavy oil, but recently the group has begun to apply the technology to bitumen from oil sands.

In a paper presented at the recent GOEXPO 11 Conference, the authors reported the removal of 98 percent of the sulphur and over 80 percent of the nitrogen from a California heavy crude with 1.54 percent S and 0.76 percent N in experiments conducted at the bench scale level.

Metallic sodium used as reducing agent

Ceramatec's technology utilizes metallic sodium to serve as the reducing agent and heteroatom scavenging agent. Either hydrogen, methane or other hydrocarbons may be used to cap radicals formed in the process. In the experiments mentioned above, the results were nearly the same when sodium was the reducing agent and when methane was used instead of hydrogen as the radical cap. Using methane instead of hydrogen is advantageous for several reasons including lower material and capital costs, greater product yield, and lower CO_2 emission.

During the upgrading process, the API gravity increases with the removal of sulphur and nitrogen and remains nearly the same when using methane as a radical cap in place of hydrogen.

When hydrotreatment with heterogeneous catalyst is the upgrading method, aromatic organics generally must become saturated with hydrogen before the C-S or C-N bonds will be broken and permit the reaction to form hydrogen sulfide and ammonia. The Ceramatec team has found considerable aromatic constituents remaining in the product, after treatment with sodium and removal of sulphur, nitrogen and metals. Since aromatic saturation is not required with sodium, considerably less hydrogen is required to obtain the same level of clean-up. Reducing hydrogen requirements reduces CO_2 emissions, because CO_2 is emitted in the steam methane reforming (SMR) process where hydrogen is produced.

Investigating the amount of CO_2 emitted from hydrogen production, Spath and Mann of the National Renewable Energy Laboratory estimate 11.9 kg CO_2 are emitted for every kg hydrogen produced taking into consideration the SMR process, and CO_2 emitted from natural gas production and transportation.[2] Using this figure, approximately 71 kg CO_2 is emitted per barrel of upgraded bitumen associated with the hydrogen required, assuming 4.5 percent S. With sodium as the reducing agent and hydrogen as the radical cap substance, the CO_2 emission drops to 20 kg CO_2 per barrel, and if sodium is the reducing agent and methane is the radical cap substance, the emission further drops to 13 kg CO_2 per barrel. This CO_2 emission is related to the production and transportation of natural gas. The difference between upgrading by hydrotreatment versus sodium/methane treatment amounts to 58,000 metric tons reduction per day per million barrels upgraded.

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Another advantage to the sodium/methane upgrading process is the incorporation of methane into the fuel. As radicals are formed with the removal of heteroatoms, hydrogen and methyl radicals are attached, resulting in mass increase relative to using hydrogen radicals alone. Instead of sending carbon into the atmosphere in the form of CO_2, the carbon is added to the liquid fuel as methyl groups and increases the energy content, mass, volume and value of the product.

Aromatics retained through upgrading

When upgrading with sodium, aromatics within the feedstock do not require saturation with hydrogen prior to removal of heteroatoms. Retaining aromatics through the upgrading process potentially can reduce the level of catalytic reforming required downstream to produce aromatic compounds to add back to the fuel product, thus operating cost and capital cost can be reduced.

Another advantage to the sodium upgrading processes, is that the total acid number, TAN, becomes negligible. For example, with a California heavy oil the TAN was reduced from 4.2 to 0. This characteristic is beneficial with regard to corrosion reduction in piping and downstream equipment. Also, the reduction in TAN assists in improving the quality of jet fuel manufactured from such a feedstock.

Earlier, experimental results matched model predictions very well except when the full amount of sodium was charged to react with the feedstock according to the sulphur and nitrogen content. The current model matches experimental results at all levels of charging for heavy oil. For example, if half the theoretical amount of sodium is used, the API gravity rises half as much as when the full amount is used. As the Ceramatec team begins to experiment with bitumen, the model predictions are matching as well. These results will be published upon completion. At this time, the results are very encouraging. Upgrading of bitumen is matching the model and upgrading is proceeding without coking.

Upgrading with sodium requires a process for the recovery of sodium from the sodium salts generated in the process. The team at Ceramatec has successfully developed this process. The recovery process is electrolytic and utilizes a sodium ion conductive ceramic membrane (NaSICON) developed and produced by Ceramatec. Cells operated for over 2000 hours electrolyzing sodium salts, for example sulfides to form sodium and sulphur have shown no signs of degradation.

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Notes:

1. J.H. Gordon, J. Alvare, M. Karanjikar, T. Dear, "Heavy Oil Upgrading Without Hydrogen," April 2011, GOEC-085.

2. P. L. Spath, M. K Mann, "Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming," February 2001, NREL/TP-570-27637