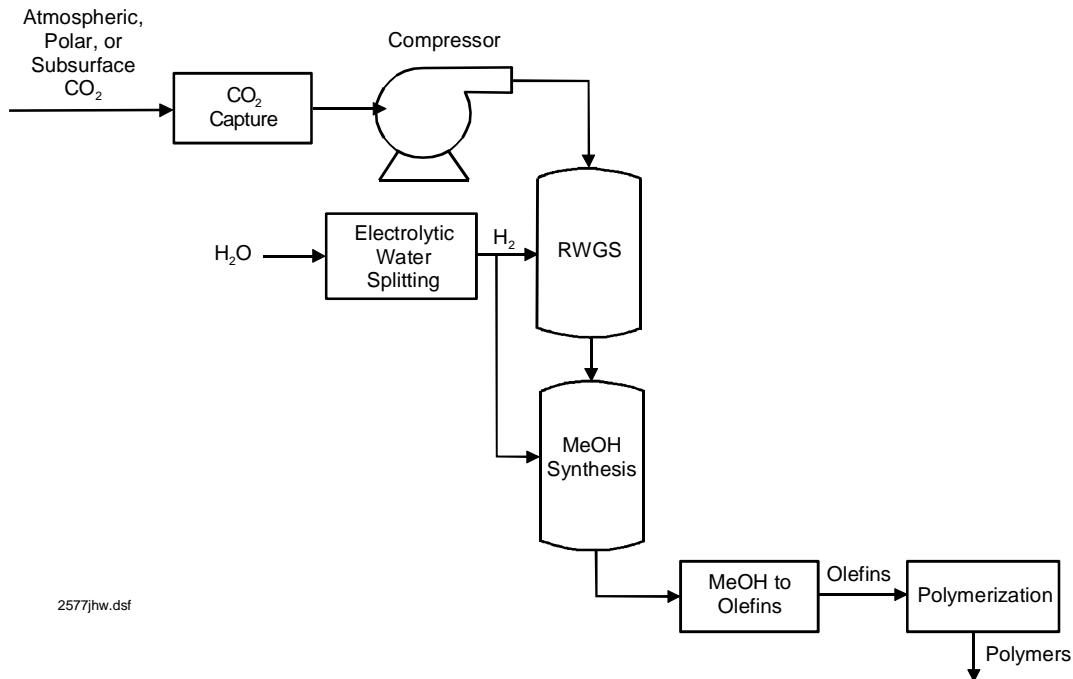




## PROCESS INTENSIFIED TECHNOLOGY FOR CONVERTING CO<sub>2</sub> TO PLATFORM CHEMICALS

Eltron has demonstrated proof-of-concept for upgrading CO<sub>2</sub> to olefins (CDTO). The process (see the **Figure** below) involving multiple steps has been demonstrated at the bench scale.



### 1. Technology Discussion

Eltron CDTO process utilizes Eltron's Reverse Water-Gas Shift (RWGS) process upstream. If the equilibrium limited RWGS system is coupled to another reaction which consumes product CO, then the equilibrium limitation can be overcome. Conversion to methanol (or DME) is one such process. Either of these oxygenates can then be converted downstream to olefins.

The thermodynamics of ethylene production itself is not onerous: ethylene production via  $2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$  is net exothermic (-72.6 kcal/mole C<sub>2</sub>H<sub>4</sub>). Unfortunately, in order to obtain 6 moles of H<sub>2</sub> (from H<sub>2</sub>O), 346.8 kcal of energy is required, thus resulting in a net energy consumption +274.2 kcal/mole C<sub>2</sub>H<sub>4</sub> or +137.1 kcal/mole CO<sub>2</sub>. However, this energy can (and must) be supplied using a non-CO<sub>2</sub> generating source. Furthermore, converting ethylene to polyethylene has a heat of reaction of -94.5 kcal/mole or 0.3 kWh/kg of CO<sub>2</sub>. In any event, a useful, valuable product, in which CO<sub>2</sub> has been sequestered, is produced. Using an integrated system which generates hydrogen from water using nuclear, solar, wind or other non-fossil fueled sources or waste heat from a nuclear power plant, coal combustion, or IGCC or IGFC system plus the above described technology, CO<sub>2</sub> can be converted to the subject platform molecules without additional emission of CO<sub>2</sub> to the atmosphere.

In the process, methanol synthesis occurs via CO from RWGS. In the conventional methanol synthesis chemistry, a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub> is reacted over a Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst and the process is highly selective to methanol, with dimethyl ether (which would be employed downstream in the overall process) being the major side product. Eltron's process benefits from tight integration in which the equilibrium limited RWGS process occurs upstream of a process going to completion (i.e., CO to methanol or DME). As shown in the **Figure** above, the process contains stages for converting CO<sub>2</sub> to methanol, methanol dehydration, and dimethylether conversion to ethylene (and propylene). These products may then be converted to polymers, aromatics, and other platform chemicals.

# Eltron Research & Development

## Tech Brief

Thus, in addition to the above steps, the system must also integrate with an upstream sub-system for CO<sub>2</sub> capture and with a downstream polymerization, aromatization, or other processing steps (depending on the products desired). While the system involves multiple sub-processes it also provides ***much more selective production of specific products***. Additionally, several of the sub-processes can be integrated by the use of bifunctional catalysts or admixtures of catalysts. Indeed, a key emphasis of Eltron's work in this area has been the identification of catalysts which can effect the desired transformation in the fewest possible steps and on process improvements which can likewise achieve greater integration while maintaining the high yields of olefins. An avenue being explored is combining RWGS, methanol synthesis, and methanol dehydration (to DME) in one step by using admixtures of the methanol catalyst and a molecular sieve catalyst which can promote both RWGS and methanol dehydration. The resulting DME could then be converted downstream to olefins. Of course, the highest degree of integration (i.e., combination of as many steps as possible) is highly desirable: We have already developed a two-stage syngas-to-olefins process in which one stage consists of syngas-to-DME and the second, DME-to-olefins.

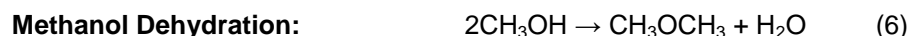
The use of microreactor technology may offer the opportunity for enhanced thermal integration and increased productivity of intermediates and products. Eltron has demonstrated the dehydration of alcohols to olefins using microchannel technology. Thus, coupling of, e.g., methanol formation and/or polymerization, which are both exothermic, with other, endothermic processes may offer further benefit to the process.

## 2. Additional Background

The starting point for Eltron's CDTO technology is its RWGS process. The RWGS catalyst is drawn from a unique family of heterogenous catalysts which have demonstrated significant activity for mechanistically related chemical transformations. These materials are based on molecular sieve supported metal clusters prepared by ion exchange of zeolite materials. These catalysts combine an electronic interaction between active site and charged support with nanoscale metal particles. The current system requires hydrogen generated via non-fossil sources or waste heat. Whatever the efficacy of this process, it is equilibrium limited so that it is essential that a downstream process be utilized for ensuring that the RWGS reaction goes to completion and that a valuable product results. Additionally, employment of the RWGS system in a loop for overall conversion of CO<sub>2</sub> to hydrocarbons via the process discussed herein can provide a net exoergic system.

The standalone RWGS system achieved equilibrium conversion of CO<sub>2</sub> at 550–600°C and atmospheric pressure, conversion of about 40% of the CO<sub>2</sub> in a stoichiometric mixture of CO<sub>2</sub> and hydrogen.

In spite of the advantages of FTS in producing hydrocarbons, the ability to directly produce a narrow range of olefinic hydrocarbon products is limited but would be very compelling, as this would reduce issues with post-processing (upgrading) and separation of products. An alternative selective route to ethylene and propylene can be found in the dehydration of methanol to olefins. This process, mechanistically related to the Mobil methanol-to-gasoline (MTG) process (Eq. 3), consists of the following series of steps:



In practice, it is desirable to carry out these reactions over one catalyst under the same conditions. This process give high methanol conversion at high combined selectivity to C<sub>2</sub> to C<sub>4</sub> olefins with ethylene being the dominant product. The use of small pore zeolite or molecular sieves, aluminophosphates (ALPOs), or silicoaluminophosphates (SAPOs) allows this high selectivity to be obtained without significant aromatics formation. Eltron has shown that at only 300°C (versus 400-450°C for the SAPO system), high (98%) conversion of methanol at 66% selectivity to ethylene and propylene can be obtained using an autoreduced molecular sieve catalyst. The use of larger pore size molecular sieves (e.g., zeolite-Y or -L) allows for the direct production of aromatics via ethylene, e.g.,



These products can also be obtained with FTS using combined FTS and aromatization catalysts.