

Catalytic Conversion of Waste Carbon Monoxide to Valuable Chemicals & Materials

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ABSTRACT

Novomer has developed a novel catalyst system that allows waste carbon monoxide (CO) and ethylene oxide (EO) to react and form useful plastics and chemical intermediates for large market opportunities. Over 2 billion metric tons of waste CO is generated globally by the steel industry, from hydrogen production, and through coal gasification. Much of this is burned as a low grade fuel which creates CO₂. The Polymer synthesized from this process is called poly(propiolactone) (PPL) and is considered by some experts to be the 'holy grail' of polymers. Novomer's catalyst can also form acrylic acid and tetrahydrofuran (THF) from waste CO. These are two chemical intermediates of great value to the chemicals industry. The former is used to make superabsorbent polymers for disposable diapers and as additives for paints and coatings. The latter is used to make spandex and as a solvent.

Keywords: green chemistry, green feedstocks, acrylic acid, acrylates, carbon monoxide, ethylene oxide, catalysts

1 TECHNOLOGY OVERVIEW

The novel breakthrough to be exploited is a new catalyst system that allows waste CO and ethylene oxide (EO) to react and form useful materials and chemical intermediates for large market opportunities. The technology has the potential to be lower cost, require less energy, and avoid CO₂. Figure 1 provides an illustration of the chemical pathways and final products. The first reaction produces propiolactone which is an intermediate to make poly(propiolactone) (PPL), acrylic acid / acrylates, or Tetrahydrofuran (THF).

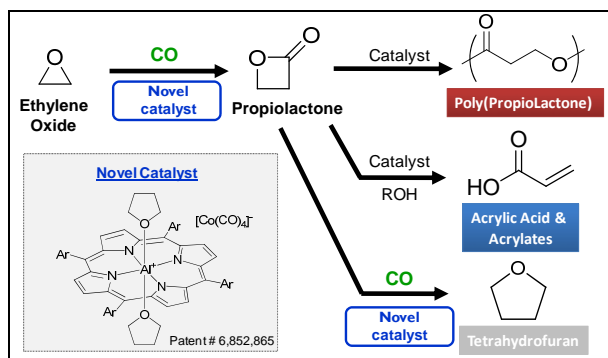


Figure 1. Novel Catalytic Technology

PPL is a potential substitute for many petroleum-based plastics like polyethylene and polypropylene, but is more environmentally friendly. It has never been produced commercially because a viable synthetic route has not been developed. Acrylic Acid / acrylates are chemical intermediates used to make diapers, paints, and coatings. THF is used to make spandex and as a solvent. The global market potential for these polymers and chemicals is well in excess of 140 Million MT/yr.

The use of carbon monoxide as a starting material by itself is not novel to the chemicals industry. CO has been used for decades as a major feedstock in the synthesis of methanol, acetic acid, and aldehydes. Additionally, since World War II Fischer-Tropsch technology has existed to react CO with H₂ to create liquid fuels. However, in most cases the CO for these processes is made on purpose from natural gas and needs to be extremely pure to achieve the desired product quality and yields. The technology proposed here would use CO that is synthesized as an undesired product in a manufacturing process and convert it to valuable materials.

2 ENVIRONMENTAL IMPACT

2.1 Greenhouse Gas Reduction

Perfecting the design and synthesis of these catalysts can impact greenhouse gases in any commercial environment where there is a stationary source of carbon monoxide that is being burned or not being used efficiently. In the following paragraphs, the hydrogen, steel, and coal/biomass gasification industries are discussed to frame the order of magnitude impact a technology could have which reduces their CO₂ footprint.

The production of hydrogen is an often overlooked source of greenhouse gas emissions and one that is likely to be growing in the future. SRI Consulting predicts that by 2011 the consumption of hydrogen will be 81 Million MT/yr and driven by ammonium production, oil refineries, and methanol plants. Of this amount 49% is synthesized from a process called Steam Methane Reforming (SMR) which according to the National Renewable Energy Lab (NREL) produces 8.9kg of CO₂ per kg of Hydrogen produced. Globally this translates to 353 Million MT/yr of CO₂ released into the atmosphere which is the equivalent of about 120 500MW coal-fired power plants. The majority of

the CO₂ in hydrogen production comes from the water gas shift reaction that converts the CO into H₂ and CO₂ (see Figure 3). A technology which can readily convert this CO into a useful product without the CO₂ byproduct will significantly reduce greenhouse gas emissions.

Steel is another industry where large amounts of carbon monoxide are produced during manufacturing. For every 1MT of steel produced about 0.5 MT of carbon monoxide is generated as off-gas (Source: New York Times, 2007). This carbon monoxide is emitted from the Blast furnace in the step where the pig iron is converted to steel. The offgas from these steps has high concentrations of CO and is usually combusted to be recovered as energy or power. However, combustion of CO is not an ideal solution because the heating value is poor compared to traditional energy gases – CO has roughly 1/5 the heating value of natural gas and less than 1/10 that of hydrogen. Additionally, when CO is combusted it produces 1.6kg of CO₂ per kg CO which is emitted to the atmosphere. On a global-scale the steel industry produces 1,300 million MT/yr of steel which emits 650 million MT of CO that equates to 1,040 MT/yr of CO₂ when combusted.

Coal gasification is a mature technology that has been around since World War II and is used to produce liquid fuels, electricity, and chemicals. It is a cost advantaged technology in some regions of the world where coal is abundant, cheap, and contributes to domestic energy security. In coal gasification the coal is converted to carbon monoxide and hydrogen in the presence of oxygen at high temperatures and pressures. Depending on the final product being produced, the syngas can be converted to a pure stream of hydrogen as in the SMR technology, burned for energy, or converted to fuels using Fischer-Tropsch technology. In almost all cases large amounts of CO₂ are produced from combustion of the CO or conversion to hydrogen (as discussed above). The DOE reports that there are 117 gasification plants globally in 2007, and, as an example, one of these can produce up to 6 Million MT/yr of CO₂ (Dakota Gasification website).

2.2 Energy Reduction

Using waste carbon monoxide as a starting material to synthesize plastics and chemical intermediates has the potential to reduce domestic energy needs by the equivalent of 150 million barrels of oil per year. Based on today's import rate of 9.8 million barrels of oil per day (Source: DOE 2009), this would reduce U.S dependence by 4%. Such a large energy reduction would contribute greatly to domestic energy security.

The preliminary energy savings attributable to the beneficial reuse of carbon monoxide can be estimated using a Life Cycle Analysis (LCA) methodology. LCA is an internationally recognized framework for measuring the complete environmental impact of a product or material from extraction of natural resources to end of use. The average energy footprint from the LCA of polyethylene (PE), polypropylene (PP), and PET is about 80 MJ/kg and is shown in Figure 2 (Source: American Chemistry Council). Using waste CO as a source of carbon in place of the petro-based feedstock for traditional polymers is expected to reduce energy consumption by about 55% in the case of PPL. If the technology achieves 50% penetration of the 135 Million MT/yr combined PE, PP, and PET global markets it will be translate to the equivalent of 450 million barrel of oil savings globally – this is three times the 150 million bbl/day that will be saved in the U.S.

Using carbon monoxide to make acrylic acid instead of the current process also contributes to a reduction in energy. However, the magnitude is not as significant because the global market is much smaller (about 3.6M MT/yr) and the energy reduction is smaller (about 15%) when compared to polymers.

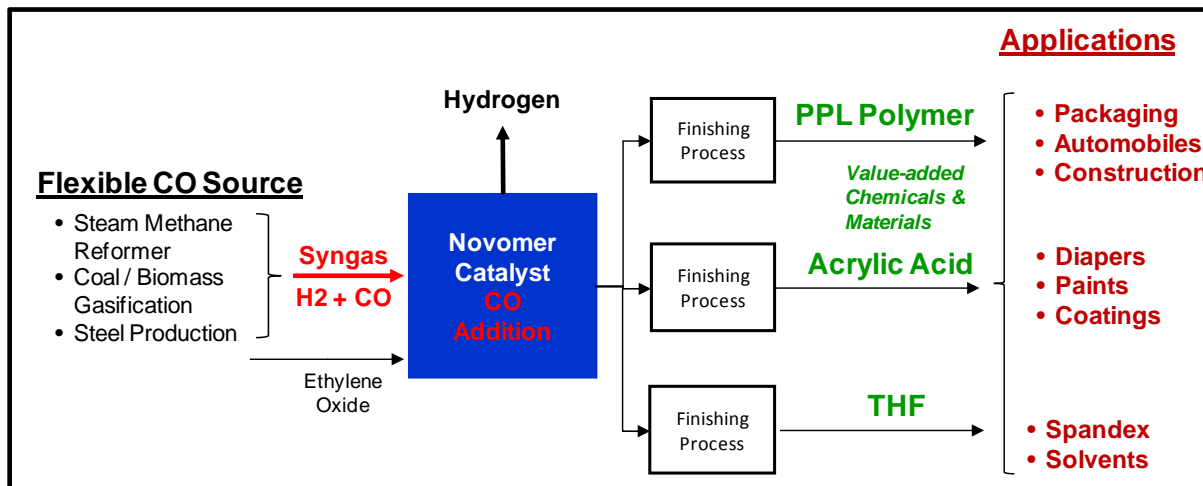


Figure 2. Utilizing Waste CO for Numerous Applications

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3 TECHNOLOGY DESCRIPTION

The technology is transformational because it allows carbon monoxide from multiple sources to catalytically react and form several materials and chemical intermediates with a broad array of applications. A schematic of the technology's potential is shown in Figure 2 above. The front-end source of CO is unchanged from current industry processes, but after that a catalyst can selectively consume the CO and leave behind pure hydrogen for use in other established applications. The CO reacts with ethylene oxide to produce propiolactone, which undergoes a finishing chemical process to produce either PPL polymer, acrylic acid, or THF. The end result of this proposed technology is that all the syngas synthesized is converted into useful, value-added products.

3.1 Syngas Flexibility

Syngas is currently used to make many different chemicals (e.g. methanol, ammonia, acetic acid) and the technology exists to use the gas in even more processes. However, one of the reasons that it isn't used is because it is expensive and costly to consistently achieve the necessary ratio of CO to H₂ for a particular reaction. Different feedstocks or starting materials will yield different syngas compositions which will produce different products if not monitored closely. The catalyst technology proposed here is syngas stream agnostic – it selectively allows the carbon monoxide to react no matter what the composition of the syngas is. This characteristic of the technology will allow feedstocks such as biomass, industrial waste, pet coke, and other carbonaceous materials to be gasified to create the above materials.

3.2 Ethylene Oxide Alternative

Using ethylene oxide as a starting material for such large market applications is also transformational and could help save an entire industry in the U.S. Ethylene Oxide (EO) is a top 20 produced organic chemical in the world by volume with global demand of approximately 20 Million MT/yr and growing. However, the U.S. global market share of EO has shrunk from a global leading position at 32% in 2003 to 22% in 2009. The main reason is new low cost production in the Middle East. Tison Keele, an ethylene oxide expert of over 20 years at Chemical Markets Associated Inc. (CMAI), provided his view on the industry during a presentation in March 2009 entitled 'Surviving the EO Train wreck'. His advice was to abandon or rationalize EO-based businesses that compete with the Middle East in markets such as MEG, or invest in new technologies which use EO to create different products. The catalytic conversion of CO and EO is a great example of a low cost route to different products that can compete globally and restore the U.S to dominance in the chemicals industry.

4 COMMERCIAL ADVANTAGES

4.1 Acrylic Acid / Acrylate Esters

Acrylic Acid (AA) and Acrylate Esters (AE) are widely used chemicals with well-documented manufacturing processes, economics, and performance requirements. The market demand of these chemicals is nearly 4 Million MT/year and is split roughly 50% AA and 50% AEs.

In terms of economics, one must consider not only material costs, but also operating and capital costs. The current state of the art for manufacturing these materials is propylene oxidation with Nippon Shokubai, a Japanese company, the predominate licensor of this technology. The Shokubai process is characterized by a highly exothermic, high temperature reaction followed by numerous separation and purification steps. The process is capital intensive and requires specialized salt cooled reactors and a complex separation process (source: Matric and Nexant, U.S. Gulf Coast basis). Manufacturing AEs requires a secondary step to convert the AA to AE through the reaction with an alcohol.

In comparison, preliminary design work indicates that a manufacturing process employing ethylene oxide carbonylation to produce AA and AEs can be simpler and lower cost from both a capital and cash cost perspective. The proposed process can be implemented in a low temperature tubular reactor, requiring less intensive separation. The use of ethylene oxide and carbon monoxide as feedstocks, results in lower capital and cash costs. In addition, the AEs can be synthesized directly from the propiolactone intermediate, avoiding the necessity of first producing and then converting AA. The comparable costs are included in the following table.

Process	Plant capacity	Capital Cost for 160KT/yr plant	Cash Cost Advantage (AA)
Current (Nippon Shokubai)	Limited to 160KMT/yr	>\$350MM	n/a
Proposed	Unlimited	<\$200MM	25%

Table 1. Acrylic Acid Process Comparisons

In addition, propylene, which used to be less expensive than ethylene, is now a more costly feedstock. Since 2004, propylene prices have been increasing relative to ethylene prices due to increasing demand for propylene based materials (polypropylene especially) and the lack of low cost of propylene containing feedstocks. Petroleum industry experts at CMAI, Inc. expect this trend to continue and there appears to be clear cost advantages associated with the proposed technology today and in the future.

In the case of performance, as these are chemicals, performance simply concerns the impurity profile. The impurity profiles of the proposed technology are expected

to be equivalent, if not better, than current materials from the incumbent process. The high degree of confidence results from the initial catalyst performance results (selectivity) and the fact that the back end of the process (rearrangement of the PPL intermediate to AA or direct conversion to AE) was performed by Celanese at a 20KMT/yr plant in Texas in the 1970's. In speaking with former Celanese employees and industry experts (e.g., Nexant Inc.), the back end process was a facile stoichiometric conversion. The reason this technology was abandoned was the poor yields and high maintenance costs associated with their process to produce propiolactone, not the conversion of propiolactone to AA.

4.2 Poly(Propiolactone) (PPL)

In contrast, Poly(propiolactone) (PPL) is a new polymer. As with any polymer, it must satisfy cost, performance, and processing requirements in order for it to successfully replace existing petroleum derived polymers.

PPL, which has shown great promise at lab scale, has not been scaled previously because economically viable catalysts to produce it have not existed prior to the discovery of the discussed technology to react CO with EO. PPL has, however, been studied extensively by the academic community, and its properties show tremendous potential. Lloyd Robeson, former employee of Air Products and current adjunct professor in Lehigh's Material Science and Engineering Department, believes PPL has the potential to be a breakthrough polymer. In a personal communication he stated that the polymer should have material properties similar to Bionelle but with raw material costs that are much lower. It would be a biodegradable polymer with the potential to be cost competitive to polyethylene. (Note: Bionelle is the PHA material that Metabolix (MBLX) is in the process of commercializing)

Preliminary cost estimates for PPL leverage the work already done for AA as the PPL intermediate is the same. Material costs and preliminary performance data for PPL appear to compare favorably to PE and PP as shown in the table below:

Critical Material Properties	Poly(propiolactone)	Petro Based Polymers (PE, PP, PET)	Bio-based PLA – PHA
Cost/Price (\$/lb)	Advantaged	\$0.80 - \$1.30	\$1.50 – \$2.50
Melting Point	75-85 °C	120-240 °C	150-175 °C
Gas Barrier	>100X better	1 (reference)	3X better
Modulus	Medium	Medium-High	Low
Impact	Good	Good	Poor
Transparency	Good	Good	Good
Biodegradable	Yes	No	Yes/No

Table 2. PPL Property Comparison