A TRULY GREEN PROCESS FOR CONVERSION OF ETHYLENE TO ETHYLENE OXIDE

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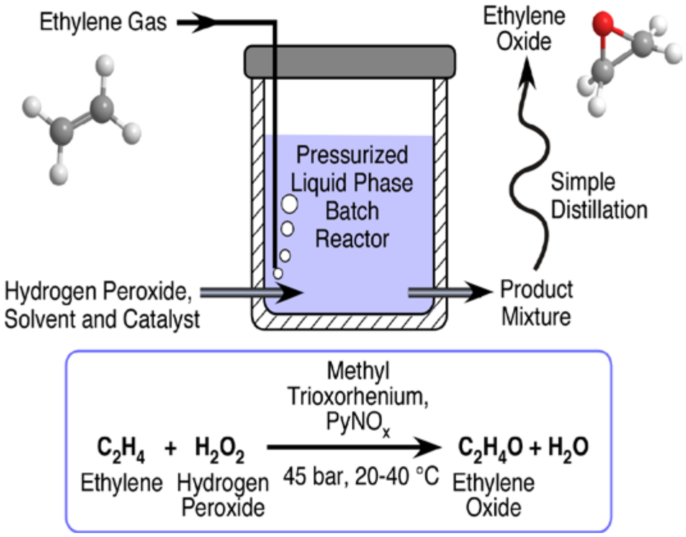

Figure 1: Schematic Summary of the CEBC Process

CONVERSION OF ETHYLENE TO ETHYLENE OXIDE

RECENT MILESTONE: The only alternative to the much modified sole and aged process used to produce over 19 million tons (year 2008) of ethylene oxide from ethylene became available through U. S. Patent 7,649,101 B2, entitled "Process for the Selective Oxidation of Olefins to Epoxides", issued January 19, 2010, with inventors Bala Subramaniam, Daryle H. Busch, Hyun-Jin Lee, and Tie-Pan Shi of the University of Kansas. While the initial discoveries leading to the processes involved conversion of propylene to its oxide, ethylene oxide production was also treated. Other relatively new processes exist for conversion of P to PO, but not for E to EO. Further, a U.S. CIP Patent Application 11/586,061, with inventors Bala Subramaniam, Daryle H. Busch, Hyun-Jin Lee, and Madhav Ghanta, focusing on ethylene oxide production by the KU process, was allowed on August 9, 2011.

QUALIFICATION FOR AWARD: The nominated technology qualifies for the Presidential Green Chemistry Academic Award (1) as the product of basic and applied research by engineers and scientists in the academic Center for Environmentally Beneficial Catalysis (CEBC) within the University of Kansas, Lawrence, KS, U.S.A. (2) Moreover, the KU process is eligible for the academic award because it provides the opportunity to decrease the production of the greenhouse gas, carbon dioxide, by replacement of the second highest producer of CO_2 from among all industrial chemical processes, which produced ~3.6 million tons in 2008 and was exceeded only by ammonia production.[1]

APPLICABLE FOCUS AREAS: Area (1) Greener Synthetic Pathways: (a) *Novel Catalyst*: In the CEBC process, high selectivity and conversion are achieved by an extremely effective, catalyst, the organometallic compound, methyl-trioxorhenium (MTO). Because many organometallic compounds are easily oxidized, it is novel to find an oxidation catalyst like MTO. Despite the obvious need for a better catalyst and process, none has been forthcoming before the CEBC process described here. (b) *Atom Economical*: this new synthesis process is atom-economical, routinely achieving 40 to 50% conversion and 99+% selectivity with no burning of substrate to produce CO_2, and an equivalent of easily managed water is the only by-product. In contrast, the traditional LeFort process (named for its 1935 inventor) must be operated at low conversion (~10-15%) to minimize substrate burning which still converts some 15% of the substrate into the greenhouse gas, CO_2.

Area (2), Greener Reaction Conditions: (a) *Energy Efficiency*: The new CEBC process operates at near ambient temperatures (20 to 40^{o}C & 45 bar; pressure benefits discussed below) compared to the LeFort process (200-260^{o}C & 10-30 bar). (b) The CEBC industrial process uses a safer and greener pathway for proposed commercial synthesis of ethylene oxide (EO) from ethylene. The established LeFort process involves heterogeneous catalysis and the gas phase and requires reliable control to avoid run-away events. In contrast, the new CEBC process uses no gas phase oxidant. The aqueous H_2O_2 oxidation occurs only in solution. (c) The reaction rate and process productivity are much enhanced by novel pressure intensification, substantially increasing the commercial promise of the process.

U.S. RESEARCH COMPONENT: Research leading to the development of this exciting new chemical process for a high tonnage industrial product has been performed in the laboratories of CEBC, a Center of Excellence of the University of Kansas (KU), with CEBC funding by federal research grants made to KU, supplemented by KU facilities and funds.

ABSTRACT: Among industrial chemical processes, the only industrial process in use for ethylene oxide (EO) manufacture (LeFort process) emits huge amounts of CO_2 (~3.6 million tons/year), exceeded only by ammonia production. This venerable gas phase technology also presents safety challenges due to the potential of explosive mixtures of gases. At CEBC we are

developing an alternative technology for the manufacture of EO, which departs dramatically from the LeFort process and satisfies several green chemistry and engineering principles. In our CEBC process, highly reactive oxidation catalyst, methyltrioxorhenium (MTO), transfers an oxygen atom from H_2O_2 to ethylene with total selectivity, high conversion, no substrate or solvent burning (to cause CO_2 emission), no explosion hazard, and, arguably, at competitive cost. Standing in contrast are the failures of modern propylene epoxidation catalysts to oxygenate ethylene. Further, despite the use of an oxidant, H_2O_2, and rhenium-based catalyst, both of which are more costly than the silver catalyst and O_2 oxidant of the LeFort system, the CEBC process is potentially economically competitive; the critical requirement is reliable in-service lifetimes of 2-3 months. The results of basic chemical experiments indicate that the CEBC system should be capable of this critical in-service lifetime. Mechanistic studies using isotopic tracers have identified the only detectable mechanism for catalyst destruction. Results suggest operating conditions to avoid that mechanism, and long term continuous process operations will soon be attempted. The relatively high productivity of this process (CEBC 40-50%; LeFort 10-15%) derives from greatly increased solubility of ethylene achieved by exploiting its own critical properties. For similar production capacities, the carbon footprint of the CEBC process is lower than the LeFort process by a net 23%; clearly showing that the benefits of no substrate or product burning are not offset by the emissions of hydrogen peroxide production. The LeFort process has undergone much innovative improvement over its many years on stream. Despite much research in many laboratories, no process has preceded the CEBC process as an economically competitive alternative to the LeFort Process. Comparing the two, the new EO process excels in conversion, selectivity, safety and sustainability, and the two appear to be comparable in manufacturing costs and productivity.

SCIENCE AND INNOVATION: The chemistry of the new technology**.** The mission of the Center for Environmentally beneficial Catalysis, led by distinguished professor Bala Subramanian, is to work with industry to catalyze replacement of wasteful and less safe chemical manufacturing processes with those that are clearly sustainable. That implies conforming to the principles of Green Chemistry, but the process must also be economically competitive. Commodity chemicals like ethylene are all *generic* in nature, with small profit margins and huge markets. It follows that success is more likely with simple straight-forward syntheses that respect Roger Sheldon's E-factor—any substrate parts not converted into the product are waste and increase product cost. The CEBC process proceeds as this requires, focusing on the transfer of an oxygen atom from a hydrogen peroxide molecule to the double bond of ethylene, producing a water molecule as by-product, and occurring with essentially complete selectivity for ethylene oxide. (See equation in Figure 1 on the Cover Page.)

This success in converting ethylene to EO is the product of an exceptional Lewis acid catalyst, methyl trioxorhenium (MTO), CH_3ReO_3, which is a very powerful electrophile because of its rhenium(VII) central metal ion. This exceptional catalyst and the novel use of *critical properties* of the substrate were responsible for the early success of the CEBC process Extensive studies of the catalytic reactions of MTO by Professor James Espenson of the University of Iowa have provided a sound basis for understanding the chemical process.[2]

An early discovery in our laboratories in the study of the epoxidation of propylene made possible the use of the critical properties of ethylene in order to vastly increase the substrate's solubility in many solvents. For the applied pressure the increase is far beyond that predicted by Henry's Law.[3, 4] Figure 2 exemplifies the data that revealed the opportunity to increase the productivity of the CEBC process for epoxidizing light olefins by pressure intensification. The

2.7 bar orange entry shows an 80% conversion in an experiment in which the dominant gas present is the substrate, propylene, in the original discovery. The same experiment under a pressure of 48 bar of CO_2 (yellow entry), including the same partial pressure of propylene, shows a substantially lower yield of product, indicating that much CO_2 has dissolved in the methanol, solvent, diluting the reaction and slowing it down. However, the same experiment, but using nitrogen instead of carbon dioxide to apply the pressure (blue 48 bar entry), results in complete conversion of the substrate into the desired epoxide product. In fact nitrogen pressure well below 48 bar still gives very high yields (red entry). The underlying fact is that within an experimentally definable number of degrees from the critical temperature, [T= (0.9-1.2)*T_C K] a non-ideal gas under pressure will exhibit exceptional solubility in solvents in which the liquid phase of the compound is soluble. This rarely used pressure intensification of solubility is a major factor in making the CEBC process for light olefin epoxidation successful and a candidate for commercialization.[4-6]

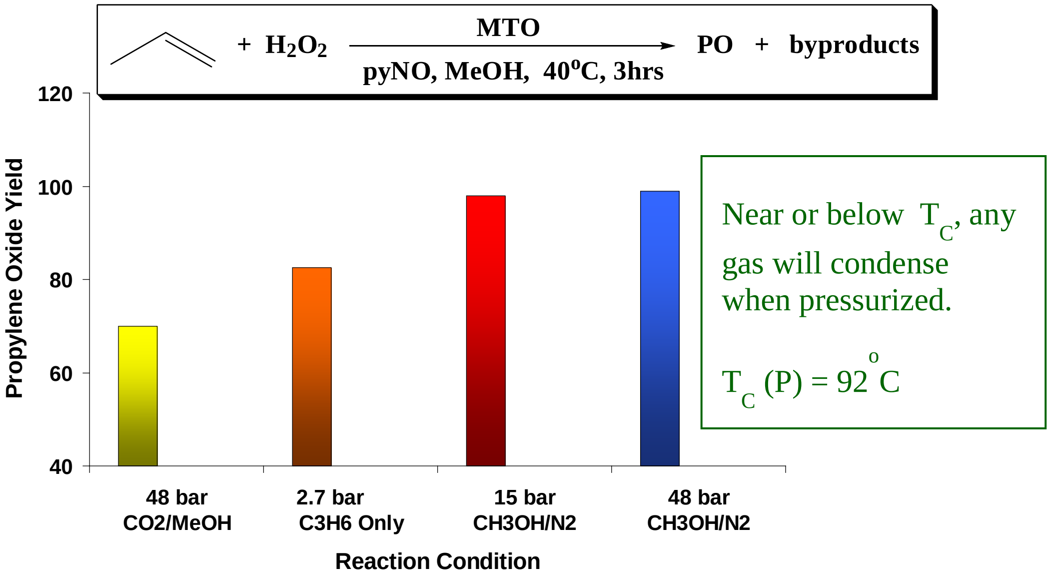

Figure 2: Pressure intensification of ethylene oxide processs ; CO_2 condenses & dilutes; N_2 condenses propylene, increasing its solubility

To become active, the rhenium atom of the MTO catalyst binds one or two hydrogen peroxide molecules, each replacing an oxide ion as a ligand of the rhenium. In the peroxo complexes, both oxygen atoms of each H_2O_2 ligand are bound to the rhenium. The coordination sphere of the diperoxo complex also includes the methyl group and an enhancer occupying two remaining coordination positions. The preferred catalyst enhancer is pyridine-N-oxide. Espenson and team explored these equilibria and related rate processes in detail, determining their binding constants, among other detailed studies.[7] Their studies also showed that, under some conditions, the catalyst undergoes a slow decomposition involving the loss of the methyl group and the catalytic activity of the rhenium species. Following the studies of Espenson, the missing detail most important to understanding the chemistry underlying the catalytic performance of MTO in the oxidation of ethylene to its oxide was "which step in the chemistry of MTO in the presence of H_2O_2 is responsible for the decomposition of the catalyst?" Experiments with labeled H_20 and H_2O_2 (in turn) in our KU laboratories[8] proved that the breaking of the CH_3-Re bond occurs in a parallel step competing with the formation of the 1:1 MTO/H_2O_2 complex. That is, in Figure 3 catalyst decomposition is associated with step one, formation of the 1:1 complex. Consequently, if only insignificant amounts of the catalyst exist in the peroxide free composition, no significant decomposition of the catalyst will occur—at least not by this mechanism. This result is of extreme importance because it profoundly affects the cost of this catalytic process. As shown in Figure 3, the formation of the monoperoxo complex from peroxide-free MTO could be minimized by excess peroxide and in turn, this would minimize the decomposition of the catalyst by forcing the diperoxo complex to do all oxidations.

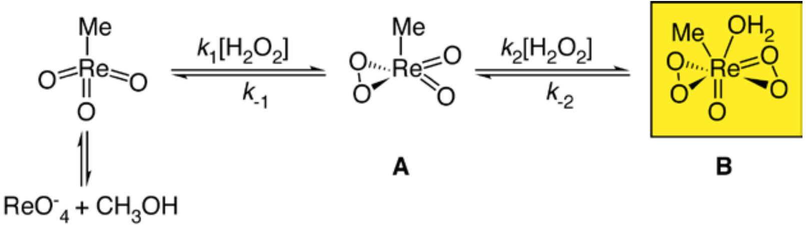

Figure 3: Mechanism for the destruction of methyl trioxorhenium catalyst

Rhenium is expensive and its MTO catalyst is difficult to make. Previously, the synthesis was both dangerous and technically challenging, but just 5 years ago, the Hermann group in Germany[9] reported a much safer method for preparing MTO from the perrhenate anion, ReO_4^-. Even with the improved recycle procedure for the MTO synthesis, the annual cost to recycle rhenium into MTO and make up small amounts of lost rhenium is estimated at $2000 and $5000, respectively. This analysis also assumes that the catalyst has an in-service lifetime of 2-3 months in order for the process to be commercially viable. The optimism that the catalyst in-service. To facilitate continuous reactions for months, we must adapt the CEBC's process for removing solvent and product from the reactor while keeping the catalyst safely inside. Such a process was developed by CEBC researchers to facilitate an advanced process for substrate carbonylations.[10]

THE PROBLEM: Environmental or Human Health Problem Addressed & Comparison with Competing Technologies**.** The new process is developed to replace the Lefort process, the only commercialized industrial process for production of EO from ethylene. The process continues to be used only because there is no alternative despite exploration of alternatives for many decades since it was first patented in 1935.[11, 12] The improvements that are inherent in adopting the CEBC process follow: (a) *Reduce Flammability or Explosion Potential*: A highly favorable feature of the new CEBC system is the fact that the MTO catalyst does not cause the decomposition of the H_2O_2 oxidant. Further, at the near-ambient operating temperature the oxidant H_2O_2 is stable. Thus, the absence of O_2 in the gas phase makes this process inherently safe. In the LeFort process, the mixture of ethylene/O_2 gases is heated to 200 to 260^{o}C to catalyze the partial oxidation of the highly flammable ethylene to produce the highly reactive EO. Safety consideration necessitates the deployment of a large volume of inert gases (N_2, Ar) to reduce the flammability envelope resulting in a significant impact on the process economics. Replacing the conventional process with the CEBC process would be like replacing the hydrogen-filled Hindenburg zeppelin with a modern jet aircraft. (b) *Reduces the Generation and Release to air of Hazardous Gases*: EO is among the largest volume products of the chemical industry. Among the large scale industrial chemical manufacturing processes, the venerable LeFort process ranks second only to ammonia production in the huge amount of carbon dioxide by-product formed. In 2008, the high temperature LeFort process, generated approximately 3.6 million tons of carbon dioxide for release into the air. The CEBC process completely eliminates the burning of ethylene and CO_2 production, thus providing both economic and environmental advantages. The productivity of the EO industry is estimated to be growing at the rate of 3-4% each year. This growth provides the opportunity to deploy this alternative technology and decrease the CO_2 released by EO production in the future. The highly selective transformation of ethylene to EO in this novel CEBC catalytic process is a powerful and important development offering the potential for the development of a more sustainable EO industry on both the domestic and global scale.

ECONOMIC ANALYSIS: Economic analysis has been performed to identify the major economic drivers in both the LeFort and the CEBC processes. Literature data was utilized to conduct plant scale simulations in Aspen HYSYS®. The mass and energy balance information obtained was used to produce cost estimations. The LeFort process is compared with the CEBC process in which (a) the *hydrogen peroxide* is synthesized by the direct H_2O_2 process (pilot-plant scale demonstrated by Udhe and Evonik Degussa Inc.), (b) the excess heat of reaction is removed by cooling water, (c) the unreacted H_2O_2 is *safely decomposed* before the reactor effluent is sent for EO recovery. H_2O_2 tends to form an explosive mixture in a distillation column and alternative H_2O_2 recovery technologies are not available.

Capital Costs: The total capital costs for both the LeFort process and the CEBC process are, within the uncertainty of this preliminary analysis, ~$120 million. The pump and compressor costs in the two processes are similar (Table 1). For the LeFort process, in addition to ethylene, large volumes of inert gases are compressed to reactor pressure. In contrast, in the CEBC process, ethylene is compressed to a higher pressure making its compressors and pumps more expensive. (a) *Distillation equipment* costs for the LeFort process are ~$ 4.5 million compared to ~$2.5 million for the CEBC process. (b) *Reactors:* both require stainless steel (SS304) for the CEBC process, costing $22 million, compared to $11 million for LeFort's carbon steel. (c) *Heat Exchanger and Cooling* equipment in the CEBC and LeFort process are $6 million and $15 million, respectively. The solvent in the CEBC case serves as a heat sink whereas LeFort process requires water cooling. (d) *Direct installation costs* for the LeFort process and CEBC process are $51 million and $13 million, respectively. Inherent design safety of the CEBC process alleviates some safety concerns and reduces instrumentation and installation costs. Further, in the CEBC process, the bulk of the unreacted ethylene is recovered by simple depressurization compared to multiple large separation columns needed to recover the unreacted ethylene in the LeFort process.

Table 1. Capital Costs in the LeFort and CEBC Process

Equipment	Lefort Process, US $Million	CEBC Process, US $ Million
Distillation Column	4.5	2.5
Reactors	11	22
Heat Exchangers and Cooling	15	6
Direct Installation Costs	51	13

Production Costs: The total production costs associated with the LeFort and CEBC processes show, in Figure 4, that raw materials and utilities are the dominant expenses.

Raw material for the synthesis of oxidant: At a market price of 8.8 ¢/lb of H_2, the cost of synthesizing H_2O_2 is 17 ¢/lb H_2O_2 and 0.77 lb of H_2O_2 is needed to synthesize 1 lb EO by the CEBC process. In contrast, in the LeFort process, the synthesis of 1 lb EO requires 1.45 lbs of oxygen, which costs only 4.8 ¢.[13]

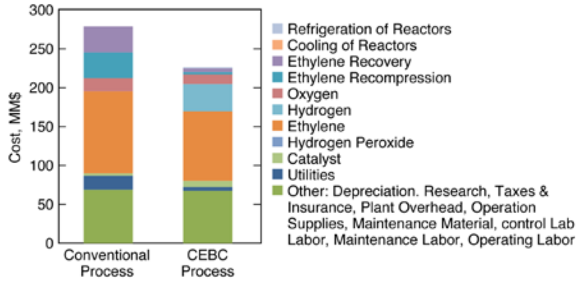

Figure 4. Production costs for EO production in the LeFort and CEBC Processes

Raw material for ethylene epoxidation: The cost of ethylene used in this analysis is 32 ¢/lb. The quantity of ethylene consumed per pound of EO is 15% higher for the LeFort process than the CEBC process due to substrate burning. Therefore higher ethylene prices in the future will have a greater adverse effect on the LeFort process. For, an ethylene market price increase from 90 ¢/lb to120 ¢/lb the change in ethylene costs incurred in the LeFort process are from $44 million/year to $ 59 million/year.

The essential recycle of unreacted ethylene and the low ethylene boiling point requires refrigeration of recovery column to -50 °C for the separation of unreacted ethylene from the Ar, CO_2, N_2 and CH_4 diluents and costs $ 60/GJ of heat removed. This complex ethylene separation in the LeFort process costs 12 ¢/lb EO. In contrast, the recovery of the unreacted ethylene from the CEBC process occurs by simple depressurization, drastically reducing refrigeration costs associated with separation. The CEBC ethylene stripper is cooled to -30 °C (costs $30/GJ of energy removed) to recover ethylene at a cost of 1.8 ¢/lb EO.

Utilities: The LeFort process employs cooling water to remove the heat of reaction. At the high operating temperatures of the process, the coolant vaporizes to form medium pressure steam at 150 psig which can be utilized to partially serve the steam requirements of the process thereby lowering the utility costs. In contrast, the mild operating temperatures employed in CEBC process offer no such advantages. The net quantity of steam consumed in the LeFort process is 3.6 lb compared to the 6.7 lb needed in the CEBC process. The cost of utilities for the CEBC process is 6.7 ¢/lb EO compared to the 2.3 ¢/lb EO in the LeFort process.

Catalyst: Rhenium at $3,000/lb makes the CEBC catalyst relatively expensive, versus $ 455/lb for the silver catalyst used in the LeFort process. Hence, near-quantitative recovery of the rhenium catalyst is essential for CEBC process viability.

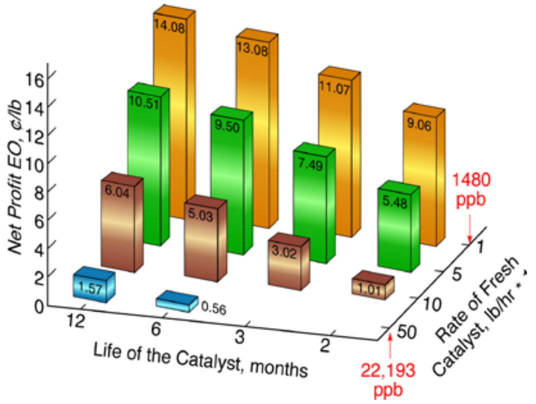

Figure 5. Effect of catalyst life and leaching rate on profitability of CEBC

Sensitivity Analysis on the catalyst life and leaching rate: The LeFort process has a profit margin of 5 ¢/lb EO. The CEBC process has the potential to be cost competitive provided the optimized MTO catalyst is active for 2-3 months and the catalyst replacement rate is less than 10^{-5} lb/h. In this analysis, we assumed that 99% of the deactivated metal is recovered and the cost of fresh catalyst and its reconstitution are $5000 and $2000 $/lb, respectively. Figure 5 shows the expected approximate trend, how an increase in catalyst inactivation lowers the competitiveness of the CEBC process, and that the profitability in the CEBC process is dependent on the near quantitative recovery and recycling of the inactivated catalyst.

CRADLE TO GATE "LIFE CYCLE" ASSESSMENT (LCA): EO is a fungible chemical commodity. Thus, the environmental impacts of both the processes are compared over a cradle-to-gate LCA. This U.S. specific LCA is performed utilizing GaBi® software and this analysis meets the ISO 14040 standards.[14] All direct and indirect environmental impacts associated with raw material production and processing are incorporated in this analysis. The boundaries of this analysis include raw material extraction, transport, processing of raw material to produce products. The mass energy balance information is obtained using Aspen HYSYS simulations. This analysis quantifies the impact of producing *23,500* kg/h of EO by the conventional LeFort and CEBC processes.

Acid Rain: The acid rain potential of the CEBC process is lower than the LeFort process by 5%. The major "hot spot" in the CEBC process, the production of methanol, requires synthesis gas which is from steam reforming of natural gas. The catalysts for steam reforming require gas purification because of extreme sulfur sensitivity. The inherent safety of the CEBC process eliminates the need for Ar, N_2 or CH_4 diluents and the absence of ethylene and EO burning eliminates the need for CO_2 absorbents. Further, the low ethylene feedstock requirement for the CEBC process is due to high selectivity towards EO. The raw material savings which translate into energy saving offset the acidification caused during the energy generation for the CEBC process to remove the excess heat of reaction.

Global Warming Potential: The *carbon footprints* associated with the production of 23,000 kg of EO by the LeFort and the CEBC process are 175,600 and 132,400 kg CO_2 equivalent, respectively. The deployment of the CEBC process reduces greenhouse gas emissions (GHG) by 23% for a 200,000 metric tonnes/year plant. GHG emissions associated with the production of H_2O_2 and methanol are clearly offset by the savings associated with the elimination of burning, manufacture of inert gases (CH_4, CO_2, Ar), and CO_2 absorbents ($KHCO_3$, K_2CO_3). Further, the savings associated with reduced ethylene inventory and power consumption in the CEBC process amount 33,515 kg CO_2 equivalent.

Water pollution is higher in CEBC process than the LeFort process by 14% because of the complexity of the materials used in the CEBC process, and the processing, origins, and impacts involved. Summarizing the major factor--natural gas is used to make synthesis gas which is required for methanol production and the natural gas is extracted by hydraulic fracturing of shale rock. Much methanol is used for safe handling of flammable hydrogen and oxygen needed for H_2O_2 synthesis. Moreover, process steam production also ties the CEBC process to water contamination. In contrast, the steam requirement in the LeFort process (high operating temperatures) is mostly met by the high pressure steam produced during the removal of the excess heat of reaction which helps lower the environmental impact in this category.

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