New Ways to Make Old Chemicals

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Introduction

Academic and industrial chemical engineering research is evolving away its roots in petroleum and petrochemicals and is moving toward new applications in growth areas such as biotechnology and materials processing. This transformation is driven in part by the general realization that major improvements in petrochemical processes are difficult to achieve because these processes have been continuously improved for decades. A few engineering firms have become the repositories of process technology for petrochemical commodities. Competitive forces drive these firms to continuously make incremental improvements in their respective technologies, but not to replace them. Steam cracking of hydrocarbons to produce ethylene is a prime example of a mature petrochemical process.

Ethylene is the world's largest organic chemical with a worldwide production of approximately 100 million tonnes per year in about 275 plants. Ethylene manufacture is dominated by steam cracking, a process that has evolved significantly in plant size and energy efficiency from the end of World War II until the present. Plant size has increased two orders of magnitude from 10,000 tonnes per annum to more than a million tonnes per annum (Kniel et al., 1980 and SRI, 2000). In the same period, the energy required to produce the chemical has dropped by a factor of 3 (Cole, 1996).

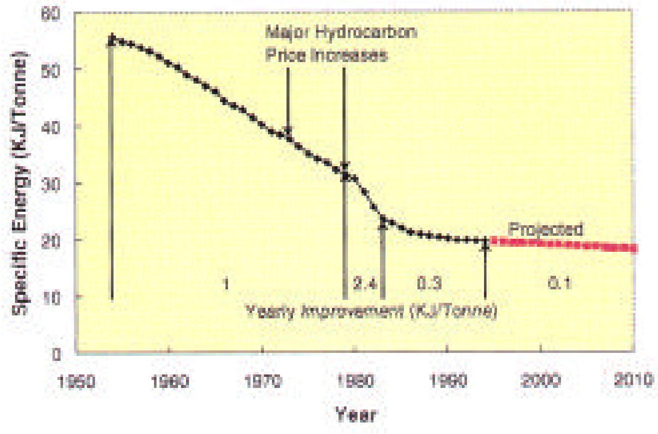

Figure 1. **Ethylene plant specific energy consumption (adapted from Cole, 1996).**

However, no immutable limit imposed by the laws of nature has been reached. Instead, materials are a key limitation. The metal upper temperature limit in the cracking furnace coils is a current limitation of the technology that is difficult to overcome. Asimilar limit in the Rankine cycle for power generation has resulted in the rise of combined Brayton and Rankine cycles. We suggest that, in spite of the success of the ethylene process, there is considerable room for ingenuity to produce major performance improvements. Historically, many established processes have been extensively modified and then replaced. The new processes usually involve significant changes to existing technology because most evolutionary changes are incremental in nature and their effectiveness eventually diminishes. The evolution and revolution in petroleum refining is a notable example of these processes. Continuous modest improvements in distillation and other unit operations in the refinery have taken place over time. These improvements have been punctuated by major process reconfigurations as thermal cracking and later catalytic cracking were introduced to maximize gasoline production and, consequently, refinery product value (Nelson, 1958). In contrast, steam cracking has only undergone evolutionary changes that appear to be slowing as evidenced by the reduction of the specific energy requirement overtime shown in Figure 1. The ethylene furnace has undergone modifications to improve product value, energy recovery, and capital cost but there has been no fundamental change in the way the ethylene is produced. The longevity and commercial success of the ethylene furnace is a testament to its effectiveness, but not its immortality.

To illustrate the possibility of revolution, we describe results from our laboratories that show that it is possible to attain selectivity and conversion from the autothermal partial oxidation of ethane that are comparable to or superior to steam cracking. This is accomplished by adding hydrogen in a 2/1 H_2/O_2 ratio to the stoichiometric 2/1 C_2H_6/O_2 composition using a platinum-tin (Pt-Sn) catalyst in a short contact time autothermal chemical reactor. This process has new degrees of freedom, since it is catalytic in nature and does not depend on heat transfer during the reaction. Thus, the materials limitations of steam cracking coils are replaced by different materials limitations of the catalyst. The detailed mechanisms of this process remain to be elucidated because most of the reaction occurs in $\sim 10^{-4}$ s in the first millimeter of the catalyst. These results are the product of an especially fruitful partnership between industry, the national labs, and academia.

What is required in a new process?

Revolutionary process changes in the chemical industry have occurred repeatedly. HCN is especially pertinent in the context of this research. It was made commercially by the reaction of sodium, coke, and ammonia to produce sodium cyanide and acidified with sulfuric acid to produce hydrogen cyanide at temperatures as high as 850°C (Wittcoff and Reuben, 1996, pp. 294–295). The process had to deal with solids, liquid, and gas phases as well as reactive and dangerous materials.

Around 1930, Andrussow developed a new process in which a selective autothermal catalytic reaction over a platinum gauze converts methane, ammonia, and oxygen into HCN and water (Thomas, 1975). This "internal combustion" process is much less expensive to construct and maintain than its predecessor, because the chemistry is many times faster and the reactor is quite simple. (Changing the reactants to ethane, hydrogen and oxygen, and modifying the catalyst slightly produces the ethylene results described in this article.) There have been similar revolutions in other processes (e.g., ethylene oxide and acrylonitrile) (Wittcoff and Reuben, 1996, pp. 110–111). While each successive process change for a given product is more difficult, imagination is only constrained by laws of nature.

Table 1. Selectivities and Conversions in Ethylene Formation from Ethane*

Process/ref.	Year	S_{C2H4}	X_{C2H6}	COx	Comments
Dehydrogenation	(1920)	60%	50%	—	Early experiments
	(1995)	85	65	0.1%	Evolved steam cracking
Autothermal Partial Oxidation					
Font-Friede	(1990)	65	70	25	Pt and Pt/Pd on ceramic foam support
Huff and Schmidt	(1993)	64	80	24	Pt on ceramic foam
Yokoyama et al.	(1996)	69	72	22	Pt-Sn on ceramic foam
Bodke et al.	(1999)	83	75	5%	Pt-Sn with hydrogen addition

*Partial oxidation data are for 2/1/0 or 2/1/2 $C_2H_6/O_2/H_2$ with feed gases at 25°C.

Ultimately, any new process must demonstrate signficantly better economics than the existing process. The demonstration is often in the form of an operating unit of a size similar to the current production unit of the existing technology. Current conventional ethylene furnaces produce on the order of 100 kilotonnes of ethylene per annum. Thus, a new technology would need to produce about this quantity of ethylene to convince manufacturers of the viability of the process.

Additionally, the process reliability, safety, and environmental performance of the new process must be at least comparable to or superior to the existing process.

What is steam cracking?

The established ethylene production technology, "steam cracking", is a pyrolysis process in which a light alkane or hydrocarbon mixture obtained from natural gas or petroleum processing is heated in metallic tubes inside a furnace in the presence of steam to a temperature at which it thermally decomposes. For ethane the primary reaction is dehydrogenation

$$C_2H_6 \rightarrow C_2H_4 + H_2,$$

Other free radical reactions also occur including continued dehydrogenation to form acetylene and association and disassociation reactions that form propylene, butadiene, benzene, and methane. These reactions require a residence time of about a 0.1 to 1 s and are endothermic. Hydrogen and methane byproducts are separated and burned in the furnace to drive the chemistry. Two very undesired reactions in pyrolysis form coke

$$C_2H_6 \rightarrow 2C_s + 3H_2,$$

$$C_2H_6 \rightarrow C_s + CH_4 + H_2$$

Coke deposits on the tube walls and necessitates periodic shutdown to burn off the carbon, further stressing the tube materials. Carbon formation is slowed considerably by adding steam that promotes the reaction

$$C_s + H_2O \rightarrow CO + H_2,$$

and so the process is called "steam cracking".

The ethylene in the furnace effluent gas mixture must be extensively processed to produce an essentially pure product (99.9%) suitable for further processing to plastics or other ethylene derivatives. No less than 19 major process systems, in addition to utilities, refrigeration systems, and storage and delivery equipment, are required to produce polymer grade products from naphtha feed (Kniel et al., 1980).

What is autothermal partial oxidation?

In contrast, autothermal partial oxidation is the alternative to steam cracking discussed in this article. In this process a hydrocarbon feed (e.g., ethane), oxygen and hydrogen in molar ratios of about 2/1/2 are fed to a catalyst zone a few centimeters thick for approximately 1 millisecond. The catalyst heats to incandescence by oxidation reactions, and the reaction is sustained (as in a fire) without heat addition or removal. The desired reaction is

$$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$$

but many other reactions—some leading to carbon oxides—occur.

The process requires an almost insignificant quantity of catalyst in a simple reactor with modest amounts of oxygen and recycled hydrogen in lieu of a complex and expensive ethylene furnace. The downstream product recovery equipment is similar to conventional steam cracking as the ethylene product must be purified in either case.

Table 1 illustrates carbon atom selectivities (percentage of feed carbon atoms appearing as ethylene in the reactor product stream) and feed conversions typically obtained. Steam cracking performance has improved considerably over time, such that now steam crackers typically obtain ~85% ethylene selectivity at over 60% conversion of ethane. Selectivity is important because it represents the fraction of feed that appears as valuable products. Conversion is also important (although less so) since the unreacted alkane is recycled after cryogenic separation, an expensive process.

High ethylene selectivity in autothermal partial oxidation

Approximately 12 years ago, Font-Friede et al. (1990) of British Petroleum (now BP Amoco, BP) discovered that approximately 65% selectivity of ethane to ethylene could be produced by reacting ethane with oxygen using platinum deposited on relatively low surface area supports. They also found that adding hydrogen to the feed improved the ethylene selectivity to about 72%, but the catalysts platinum and platinum-palladium used by BP were not nearly as sensitive to hydrogen addition as the ones reported here.

At University of Minnesota, partial oxidation of alkanes has been explored in autothermal reactors for many years. It was been proposed to produce syngas (Hickman and Schmidt, 1993), olefins (Huff and Schmidt, 1993; Yokoyama et al., 1996; Bodke et al., 1999, 2000) and oxygenates (Goetsch and Schmidt, 1996) using many different catalysts and conditions.

Minnesota experiments on ethylene production from ethane feed duplicated the BP results using low surface area ceramic foam monolith supports at catalyst contact as low as 10^{-3} s. The contact time and catalyst geometry were similar to that used for many years for HNO_3 synthesis by NH_3 oxidation and in HCN synthesis by ammoxidation of CH_4 (Schmidt and Hickman, 1993). A few years later, it was discovered that the selectivity could be increased from 65 to ~70% by adding tin or other elements to platinum, but this was still well below the 85% selectivity of steam cracking.

Several years ago, Minnesota and The Dow Chemical Company began a collaborative research program to see if there might be ways to improve the performance of partial oxidation to compete with steam cracking. We tried varying many parameters and scaling up the process from a 3/4 in. diameter to a 4 in. diameter reactor to see how the process changed with size. Results were quite reproducible and were easily scaled up, but the performance was never much above 70% selectivity. One possibility that we explored was adding hydrogen to the Pt-Sn catalyst. The selectivity jumped to about 83% at a feed conversion of 75%.

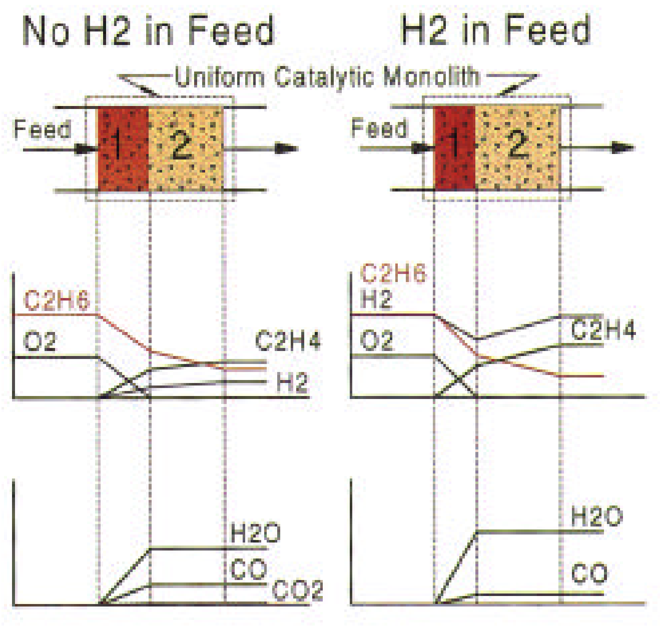

Figure 2. **Molar flow profiles for two zone reaction model without and with hydrogen in the feed. Feed flows over an autothermal, uniform, catalytic monolith. In Zone 1 (aerobic), catalyst initiated partial oxidation reactions dominate. In Zone 2 (anaerobic), gas phase dehydrogenation is the major reaction. Residence time is ~1 millisecond.**

Why does hydrogen produce a large increase in selectivity?

A simple explanation for the hydrogen induced selectivity increase of the Pt-Sn catalyst is that it simply catalyzes hydrogen and oxygen combustion and suppresses oxidation of C-C bonds in the hydrocarbon feed. In this scenario, the hydrocarbon has little interaction with the catalyst, and ethylene is produced by dehydrogenation in the hot steam generated by the hydrogen combustion. Diffusion theory supports this explanation. The flux of H_2 to the catalyst surface is ~4 times that of C_2H_6, because it is an inverse function of the square root of molecular weight (Smith, 1970). This allows the H_2+O_2 reaction to dominate at the surface, leading to only ~5% CO_x. Replacing feed hydrogen with deuterium also supports this explanation, since it has been observed that most of the water formed contains deuterium and most of the product molecular hydrogen does not (Bodke et al., 1999). However, there are two problems with this simple explanation. (1) Some catalysts produce predominately carbon oxides with or without hydrogen present in the feed; (2) simple dehydrogenation is too slow to form the observed amounts of ethylene.

The first problem may be explained by asserting that, unlike non-hydrogen sensitive catalysts, platinum-tin keeps the active platinum clear of adsorbed oxygen and reduces the likelihood that the hydrocarbon can be attacked by multiple oxygen atoms leading to carbon oxide formation. The second problem may be explained by asserting that the catalytic surface generates active species that increase the rate of gas-phase reactions.

Possible concentration profiles of various species are indicated at the top of Figure 2. Without H_2 added, a significant amount of C_2H_6 is oxidized, leading to the observed 25 mole % CO_x in the reactor product.

We and others (Bodke, et al., 1999 and Zerkle, et al., to be published) are attempting to model this process in order to understand the mechanism and possibly improve catalyst performance. A satisfactory model will require detailed heterogeneous and homogeneous reaction chemistry coupled with full two dimensional fluid mechanics and complete thermodynamic properties of the gas mixtures. More simple models do not match experimental results. Heterogeneous-only models under-predict olefin formation. Homogeneous-only models under-predict conversion. It is obvious that this is a particularly difficult problem to model because all reaction is complete within ~10^{-3} sec, the axial and radial gradients in temperature and concentration are extremely large, and the reaction rates in the two phases are not known in detail.

Will autothermal partial oxidation displace steam cracking?

Our current results show performance comparable to that of steam cracking for ethylene by autothermal partial oxidation of ethane (Figure 3). Experiments are in progress to examine these reactions with higher alkanes. This process requires a residence time that is ~2 orders of magnitude less that used in steam cracking and eliminates the need for a tube furnace, a major capital cost component in a steam cracker. Thus, the capital cost is less than that of steam cracking. Each process appears to require about the same quantity of ethane, but the autothermal alternative requires pure oxygen. Also, the raw materials cost is higher than for steam cracking. The products formed in autothermal partial oxidation are similar to those produced in a steam cracking furnace, so that the separation requirements can be handled by existing technologies. Recycle of H_2 is required, but this is now done in steam cracking for fuel to drive the furnaces.

This is the classic economic analysis problem of the balance between captial cost and raw material cost. Careful analysis will be required to ascertain the relative value of the two processes.

Assuming the autothermal process is economically superior, there are still many hurdles to developing a process to replace steam cracking, including environmental and operational performance.

Recent global climate change information has generated concerns over greenhouse gases such as carbon dioxide. Autothermal partial oxidation does not directly generate as much CO_2 as conventional ethylene furnaces. However, inclusion of subsequent combustion of the byproduct fuel and electricity generation for oxygen separation results in comparable CO_2 emissions for each process. NO_x generation is less for autothermal partial oxidation than steam cracking. The oxidation reactions occur in nitrogen free atmospheres in the autothermal reactor and in highly controlled power generation equipment for oxygen separation instead of the high-temperature cracking furnaces. Water generated in the autothermal process is condensed and discharged as liquid instead of as vapor from the cracking furnace stack, so the water treatment system load will increase.

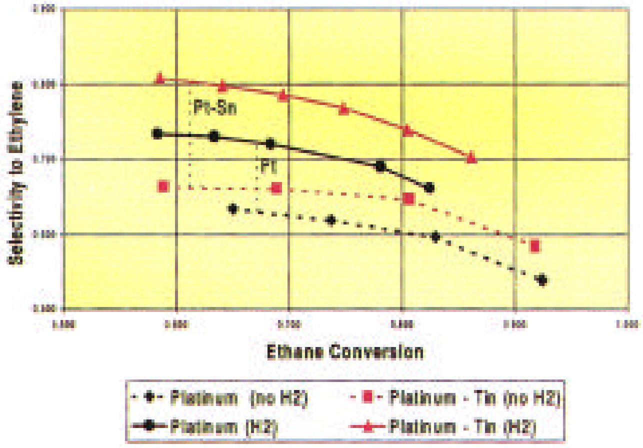

Figure 3. **Carbon atom selectivity to C_2H_4 as a function of C_2H_6 conversion. Results are shown for Pt and Pt-Sn catalysts on alumina foam monoliths at ~1 millisecond contact time. Addition of 1 mole H_2 per mole C_2H_6 to either the Pt or Pt-Sn catalyst results in a substantial selectivity increase.**

Process safety is of paramount importance in huge petrochemical plants. Mixing oxygen and hydrocarbons requires very stringent operating discipline to prevent the possibility of explosion and fire. Conventional steam crackers combust massive amounts of hydrocarbon fuel using a system of controls that operate reliably and automatically. Asimilar control system will be necessary for the autothermal partial oxidation process. Just as a burner in the cracking furnace is fed with fuel as long as a flame is determined to be present, the autothermal reactor can be fed oxygen as long as the catalyst remains incandescent. Additionally, ethylene oxide is produced with a hydrocarbon (ethylene) and oxygen feed over a catalyst and the previously mentioned HCNand nitric acid processes have operated safely for many years with similar catalysts and combustible feeds.

To sum up

The history of the process industry might be described as "punctuated evolution" to borrow a phrase from life sciences. A design will be steadily improved from prototype to elegant efficiency only to be displaced by a fundamentally superior approach. In each cycle the difficulty increases, because of the success of the last cycle. However, we suggest that revolutionary improvements are possible in even very sophisticated technologies. Revolution will continue because scientists and engineers are never satisfied. They are driven to make things "better, cheaper, and faster".

This new olefin technology is a recent example that may or may not prevail, but ultimately there are new ways to make old chemicals and they will be discovered.

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