



# **Greenhouse Gas Emissions from New Petrochemical Plants**

**Background Information Paper  
for the Elaboration of  
Technical Notes and Guidelines  
for IDB Projects**

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**Inter-American  
Development Bank**

Environmental  
Safeguards Unit

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This Technical Note was prepared by the Environmental and Social Safeguards Unit (VPS/ESG) of the Inter-American Development Bank (IDB). ESG works to promote the environmental and social sustainability of Bank operations. It collaborates with project teams to execute the IDB's commitment of ensuring that each project is assessed, approved and monitored with due regard to environmental, social, health and safety aspects, and that all project – related impacts and risks are adequately mitigated or controlled. ESG also helps the Bank respond to emerging sustainability issues and opportunities.

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## List of Acronyms

ATR	Autothermal Reforming
BAT	Best Available Technology
bbl	Barrel
BF	Benchmark Factor
BIC	Best-in-Class
btu	British Thermal Unit
CAPEX	Low Capital Expenditure
CF	CO <sub>2</sub> Emissions (t CO <sub>2</sub> /t HVC)
CGC	Cracked Gas Cooling
CHP	Combined Heat and Power
E&P	Exploration and Production
EF	Emissions Factor (MT CO <sub>2</sub> /GJ)
EJ	Exajoule (EJ) = 10 <sup>18</sup> J
EPA	Environmental Protection Agency
FCC	Fluid Catalytic Cracking
FIP	Federal Implementation Plan
GHG	Greenhouse Gas
GJ	Gigajoule (GJ) = 10 <sup>9</sup> joules
GJ/t	Gigajoule Per Ton
GWP	Global Warming Potential
HC	Hydrocarbon
HDPE	High Density Polyethylene
hp	Horsepower
HTS	High Temperature Shift
HVC	High-Value Chemical
IEA	International Energy Agency
IFA	International Fertilizer Industry Association
IFC	International Finance Corporation
ISBL	Inside Battery Limit
kcal	Kilocalorie
kg	Kilogram
kMT	Thousand Metric Tons
kPa	Kilopascal
kT or kt	Kilo Ton (1,000 Metric Tons)
kty or kt/yr	Kilo Ton Per Year
kW	Kilowatt
LAC	Latin America and the Caribbean
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LPG	Liquefied Petroleum Gas
LTS	Low Temperature Shift
MDPE	Medium Density Polyethylene
MT	Metric Ton

MW	Mega Watt
MMBtu	Million British Thermal Units
mt	Mega (Million Metric) Tons Per Year
NGL	natural gas liquid
PE	Polyethylene
PP	Polypropylene
ppm	Parts Per Million
T&T	Trinidad and Tobago
TIC	Total Installed Cost
TLE	Transfer Line Exchanger
TQM	Total Quality Management
SCB	Short Chain Branching
SEC	Specific Energy Consumption
SRT	Short Residence Time
USC	Ultra Selective Cracking
USGC	U.S. Geological Survey
w/w	Weight/Weight



## **Executive Summary**

Supporting the Latin America and the Caribbean (LAC) region in responding to climate change is emerging as a crucial development challenge for the IDB. Recently, the IDB set out elements of a strategy for Climate Change Action as a means of strengthening the Bank's efforts to respond to this challenge. One of the pillars of the strategy is to integrate climate change concerns into IDB operations by identifying and addressing the contribution of IDB-financed projects to GHG emissions in particular in emission-intensive sectors, and strengthening the safeguards aspects of climate change. As a constituent part of its climate strategy, the Bank is developing specific guidelines to: provide clear minimum climate change performance criteria for IDB support of projects, as well as guidance on assessing and managing potential impacts of projects on climate change; enhance the Bank's capacity to assess the risks and vulnerability of projects as a result of climate change; and report on the carbon footprint of its portfolio of operations.

The petrochemical industry is a growing sector in LAC. The greenhouse gas (GHG) emissions generated by the petrochemical industry can be unnecessarily high for projects that do not select and implement climate-friendly technologies, practices, and fuels.

When analyzing the environmental impacts of future petrochemical industry projects, the IDB will take into account the energy efficiency and other aspects of the projects' design and operation and their impacts on reducing GHG emissions. To conduct these analyses and to define appropriate project performance requirements, the IDB is commissioning this study to enhance its understanding of the different GHG emission scenarios for the development of the petrochemical industry in LAC, the best technology options, and the benchmarks for performance within the industry, both globally and in the LAC region.

The study encompasses background information on the relevant processing and "value chains" in the petrochemical industry within LAC, the current GHG emission control technologies available, and recommendations and relevant steps for the IDB, including the criteria to help

evaluate the potential GHG emissions from the petrochemical sector and the criteria to help determine the minimal acceptable potential GHG emissions from petrochemical projects.

This Executive Summary presents the key points and conclusions (in a bullet format) of each of the sections that are developed in the document.

## **I. General Aspects**

### **A. The Petrochemical Industry**

- The chemical and petrochemical sector accounts for approximately 30% of the total industrial final energy demand.
- The chemical and petrochemical industry generates 18% of the direct industrial CO<sub>2</sub> emissions (excluding electricity production).
- The petrochemical production capacity has practically doubled over the last 15 years, with a current capacity of 130 million metric tons per year (mt) and a demand of 114 mt.
- The production of ethylene, the petrochemical “bellwether,” has been increasing at an annual pace of 4.5% on a global basis over the last 10 years.

### **B. GHG Emissions from Petrochemical Plants**

- The Environmental Protection Agency (EPA) reports that CO<sub>2</sub> contributes about 98% of the GHGs, while CH<sub>4</sub> and NO<sub>2</sub> account for 2.25% and 0.08%, respectively.
- Estimates published by petrochemical companies such as ExxonMobil Chemical, Chevron Phillips Chemical Company LP (Chevron Phillips Chemical), BASF, and BP Chemical indicate that GHG emissions are overwhelmingly composed of CO<sub>2</sub>, while the amounts of CH<sub>4</sub> and NO<sub>2</sub> are negligible in comparison (less than 1%).
- In a petrochemical plant, CO<sub>2</sub> emissions come from three main sources:

- The fuel combustion used to heat the steam cracker furnaces (by far the largest source)
- Other energy (electricity) generation
- Feedstock or process gas losses from cracker operations

### **C. Petrochemicals in LAC**

- On a global basis, one may expect the LAC region to be one of the most active investment areas for petrochemical projects behind the Middle East and Asia.
- Brazil and Mexico are arguably the only two LAC countries that have a fully integrated petrochemical industry with a complete value chain, namely, large crude oil/gas sources, sufficient refining capacities, ethylene steam cracking capabilities, a sizable chemical processing sector, and a healthy consumer products market.
- More than 50% of LAC's ethylene capacity is in Brazil. On the other hand, Trinidad and Tobago and Chile are the largest producers of methanol, the largest-volume petrochemical in LAC.
- Latin America is a net importer of other petrochemical products—most notably propylene and butadiene.
- The new U.S. shale gas boom (i.e., fracking = hydraulic fracturing with horizontal drilling) is a “game-changer” for feedstock costs. This may become a competitive challenge to LAC's naphtha cracking plants.

## **II. Specific GHG-Intensive Industries: Design, Energy Balances, CO<sub>2</sub> Emissions**

### **A. Steam Cracker Technology, Composition, and Characteristics**

- Most of the energy consumption by the steam cracker components, other than the furnaces, is done via a combined heat and power (CHP) system (gas/steam turbo compressors), which is driven by the high temperature/high pressure process gas.

- In the pyrolysis (furnace) section of the cracker, molecules are “cracked, split, and decomposed” from large to small via a free-radical mechanism, such as dehydrogenation of ethane or naphtha.
- The pyrolysis section consumes 47% of the total energy for the ethane cracker; the naphtha cracker furnaces consume anywhere from 65% to 73%.
- A naphtha cracker is more energy intensive and emits more CO<sub>2</sub> relative to the amount of ethylene produced (per metric ton) than an ethane cracker does.
- “Scale” has a major impact on plant investment costs as well as operating costs; total initial investment costs per metric ton of high-value chemical (HVC) capacity decrease with plant capacity.
- Competing steam cracker technology vendors and licensors have comparable technologies, which would be expected as this is a very mature industry.

## **B. Polyethylene and Polypropylene**

- Polyethylene (PE) and polypropylene are the largest-volume petrochemicals produced in the world.
- Overall, there are two main manufacturing processes for producing PE, namely, low pressure and high pressure.
- The low pressure process produces linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE); the high pressure process produces low density polyethylene (LDPE).
- On average, the 2006 EU Best Practice for Energy Intensity of manufacturing plants for LDPE, HDPE, and propylene (PP) is 5.96, 3.14, and 2.27 gigajoules (GJ)/t respectively.

### **C. Methanol**

- Methanol can be produced from a wide range of feedstocks, such as natural gas, coal, biomass, agricultural and timber waste, solid municipal waste, and a number of other feedstocks.
- Methanol can be produced via three reforming technologies for the production of synthesis gas, namely, one-step reforming with fired tubular reforming, two-step reforming (a primary reforming and a secondary reforming), and autothermal reforming (ATR).
- As of 2007, a typical methanol plant uses about 30 GJ of natural gas energy to produce 1 MT of methanol; the theoretical minimum energy use (close to Best Applicable Technology) is about 20 gigajoules per ton (GJ/t).

### **D. Ammonia and Urea**

- Ammonia is synthesized from hydrogen contained in natural gas (main feedstock) and nitrogen contained in air; urea is synthesized from ammonia and carbon dioxide.
- For each fertilizer product category, more than 90% of LAC's production is concentrated in a maximum of five countries; Brazil is one of the top five producers for each fertilizer product category.
- Most ammonia manufacturing technologies are derived from the original "Haber-Bosch process."
- As of 2005, the energy intensity of methanol plants was 35 GJ/t NH<sub>3</sub>, 35 GJ/t NH<sub>3</sub>, and 36 GJ/t NH<sub>3</sub>, respectively, for Western Europe, North America, and Latin America.

## **III. Benchmarks for Future Petrochemical Plants**

- Benchmarks for ethylene steam crackers can be based on specific energy consumption (SEC), CO<sub>2</sub> emissions, and HVC yields for both the ethane-fed cracker and the naphtha-based cracker, the two most widely used feedstocks in petrochemical plants.

- Energy intensity benchmarks are suggested for PE/PP (Weighted EU Averages), methanol (Licensor “Best-in-class”), and ammonia/urea plants (Canadian Office of Energy Efficiency “Best-in Class”).

## **I. General Aspects**

### **A. The Petrochemical Industry**

#### **1. Definition, Energy Use, and GHG Emissions**

##### **a) Definition**

The petrochemical industry comprises the crude oil refining industry and the chemical industry in terms of products, flows, and value chains. Basically, some of the crude oil refinery outputs are further refined and processed to produce petrochemical products. To take advantage of economies of scale and greater logistic integration, much of the petrochemical refining and processing is carried out in a petrochemical complex where crude oil is refined. There is a good amount of literature that groups the petrochemical and chemical industries together. Strictly speaking, the petrochemical industry generally refers to the chemical products processed from hydrocarbons.

For the most important olefin, ethylene, the global growth rate is approximately 4.5%/year while the processing capacity is estimated to double again by 2025. Various alternative production routes to ethylene/propylene have been recently proposed. The bulk of new production will still come from conventional steam crackers.<sup>1</sup>

##### **b) Energy Use**

In 2006, the chemical and petrochemical sector's demand for energy and feedstocks accounted for approximately 10% of worldwide final energy demand (final process energy plus feedstock energy), equivalent to 35 exajoules (EJ)/year. The sector accounts for approximately 30% of the total industrial final energy demand.<sup>2</sup> In the overall production process, more than half of the energy demand is for feedstock use.<sup>3</sup>

---

<sup>1</sup> Bowen, C.P. and Jones, D.F. 2008. "Mega-olefin plant design: Reality now "Bigger is better," when planning future ethylene processing capacity." Houston, Texas: Shaw Energy & Chemicals.

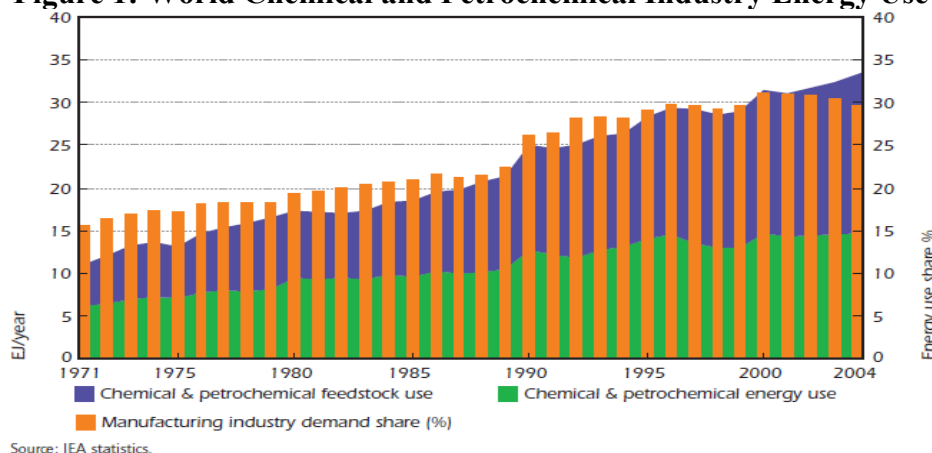
<sup>2</sup> International Energy Agency. 2007. *Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions*. ENERGY, INDICATORS, © OECD/IEA, [www.iea.org/w/bookshop/pricing.html](http://www.iea.org/w/bookshop/pricing.html).

<sup>3</sup> IEA Report. 2008. "Energy Statistics of OECD countries." Paris: OECD/IEA.

The International Energy Agency (IEA) reported that the share of the chemical and petrochemical industry in total manufacturing energy use doubled<sup>4</sup> from 1971 to 2004. This is highlighted in Figure 1.

Phylipsen et al. (2002) have<sup>5</sup> suggested a potential 20% reduction in energy intensity by using state-of-the-art technologies (regional variations of plant characteristics would account for higher figures). The IEA reported that the theoretical energy consumption using best available technology (BAT) with actual energy use suggests a 13% to 16% improved energy efficiency potential for energy and feedstock use while excluding electricity.<sup>6</sup>

**Figure 1: World Chemical and Petrochemical Industry Energy Use**



The potential is somewhat higher in countries where older capital stock predominates. When compared to the energy use of the chemical and petrochemical sector as reported in energy statistics, this potential translates to approximately 35% savings.<sup>7</sup>

### c) GHG Emissions

Based on the aforementioned IEA report, the chemical and petrochemical industry is the third-largest source of CO<sub>2</sub> emissions after the iron/steel and cement industries. It accounts for 18%

<sup>4</sup> International Energy Agency (IEA). 2006a. *Energy Technology Perspectives, Scenarios and Strategies to 2050*. Paris: OECD/IEA.

<sup>5</sup> Phylipsen, D., Blok, K., Worrell, E. et al. 2002. "Benchmarking the energy efficiency of Dutch industry: an assessment of the expected effect on energy consumption and CO<sub>2</sub> emissions."

<sup>6</sup> EA. 2007. "In support of the G8 Plan of Action, Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions."

<sup>7</sup> Saygın, D., Martin, K., Patel, Tam C. et al. September 2009. "Chemical and Petrochemical Sector, Potential of best practice technology and other measures for improving energy efficiency." IEA information paper, OECD/IEA.



of the direct industrial CO<sub>2</sub> emissions (excluding electricity production). In 2006, the process energy requirements of the chemical and petrochemical sector generated approximately 1 240 Mt CO<sub>2</sub> (IEA estimate), excluding indirect emissions from power use and from the treatment of post-consumer waste, e.g., from the incineration of plastics.

The above is only an introduction to GHG emissions. A more detailed discussion and more information about all GHG emissions (types and estimates) from new petrochemical plants are reported below.

## **2. Petrochemicals Products and Value Chain**

Petrochemical products are made from petroleum feedstock (such as crude oil) and natural gas. In general, more than 4,000 organic and inorganic chemical products are classified as “petrochemicals.”

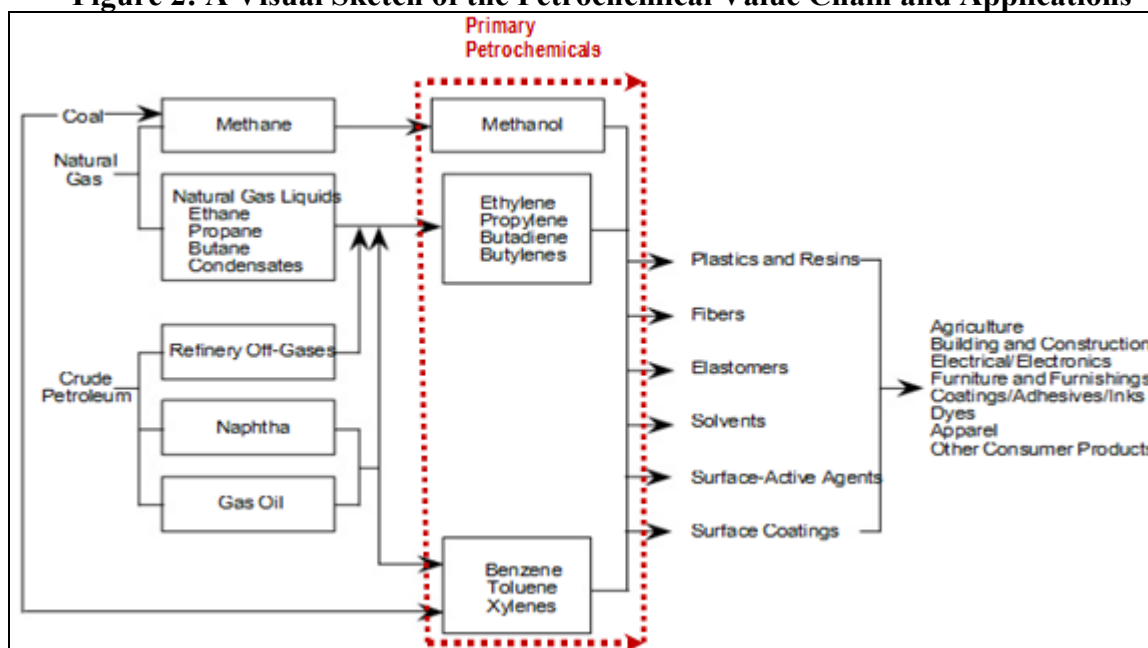
From a petrochemical industry perspective, there are three general groups of products, namely:

- Olefins (including ethylene, propylene, and butadiene), which belong to a class of unsaturated aliphatic hydrocarbons having the general formula  $C_nH_{2n}$
- Aromatics (including benzene, toluene, and xylenes), which are unsaturated cyclic hydrocarbons containing one or more rings
- Synthesis gas, which is used in ammonia and methanol

Olefins, aromatics, and synthesis gas are called “primary petrochemicals.” They are utilized to make a wide range of chemical compounds. In view of their complexity and the very high number of their derivatives, finished industrial products, and consumer applications, we will focus on the primary petrochemicals, their energy demand, and GHG emissions. This focus is also warranted due to the fact that primary petrochemicals have the highest GHG emissions (on a relative basis) in the value chain.

A detailed flow chart depicting the value chain of the petrochemicals is shown in Figure 2.<sup>8</sup>

**Figure 2: A Visual Sketch of the Petrochemical Value Chain and Applications**



Source: SRI Consulting<sup>9</sup>

### 3. Ethylene, Primary Petrochemicals, and Derivatives

Primary petrochemicals, such as ethylene, propylene, and butadiene, are utilized to form secondary petrochemicals and other chemical products. The secondary petrochemicals latter are used to produce various industrial and consumer products. Among the primary petrochemicals, ethylene is the most important in terms of production volume and HVCs. In general, the HVCs include ethylene, propylene, butadiene, and aromatics, which are the sources of most of the consumer product applications, such as plastic (bottles, bags, and packaging), insulating materials (wire, cables, and hoses), etc. Furthermore, ethylene is polymerized via chemical synthesis into high density polyethylene (HDPE), LDPE, and LLDPE.

<sup>8</sup> Ibid.

<sup>9</sup> SRI Consulting. 2011. *Chemicals Handbook*.

Typical production of ethylene, other olefins, aromatics, and other petrochemicals is shown in Table 1.<sup>10</sup> This is based on the most prevalent feedstock utilized around the world, namely, ethane, propane, butane, naphtha, and gas oil.

**Table 1: Petrochemical Production for Various Feedstocks**

Influence of feedstock on steam cracker yield (in lb for 1,000 lb of feedstock)	Ethane	Propane	Butane	Naphtha	Gas Oil
High value chemicals (HVCs)	842	638	635	645	569
Ethylene	803	465	441	324	250
Propylene	16	125	151	168	144
Butadiene	23	48	44	50	50
Aromatics	0	0	0	104	124
Fuel grade products	157	362	365	355	431
Hydrogen	60	15	14	11	8
Methane	61	267	204	139	114
Others	32	75	151	200	304
Losses	5	5	5	5	5

Source: Neelis et al. (2005)<sup>11</sup>

In Table 1, one may note that ethylene production constitutes the highest volume produced from steam cracking of any feedstock. Moreover, the two highest producers of HVCs are ethane and naphtha feedstocks. This factor and other factors—to be discussed in detail in Section II - are the main drivers for making ethane and naphtha the most widely used feedstocks in the petrochemical industry.

It should be noted that annual production of ethylene increased globally at a pace of 4% to 5% annually<sup>12</sup> from 2000 through 2010. A detailed description of all ethylene applications<sup>13</sup> and their end uses is shown in Table 2.

<sup>10</sup> Neelis, M.L., Patel, M., Gielen, D.J. et al. 2005a. “Modeling CO<sub>2</sub> emissions from non-energy use with the non-energy use emission accounting tables (NEAT) model.” *Resources, Conservation and Recycling*, 45.

<sup>11</sup> Ibid.

<sup>12</sup> Rappaport, H. May 2011. *Ethylene and Polyethylene - Global Overview*. SPI Film & Bag, <http://spi.files.cms-plus.com/about/fbf/H%20Rappaport%20SPI%20Film%20%26%20Bag%2005%2011.pdf>.

<sup>13</sup> American Chemistry Council. December 2004. *Ethylene – Product Stewardship – Guidance Manual*, [http://www.lyondellbasell.com/techlit/techlit/Handbooks%20and%20Manuals/ACC\\_Ethylene\\_Manual%203096.pdf](http://www.lyondellbasell.com/techlit/techlit/Handbooks%20and%20Manuals/ACC_Ethylene_Manual%203096.pdf).

**Table 2: Ethylene Applications and End Uses**

Product Application	% of Total Use	Application Description
<p>Polyethylene</p> <ul style="list-style-type: none"> <li>• High Density Polyethylene (HDPE)</li> <li>• Low Density Polyethylene (LDPE)</li> <li>• Linear Low Density Polyethylene (LLDPE)</li> </ul>	<p>25</p> <p>19</p> <p>13</p>	<p>Common processing options for HDPE, LDPE, LLDPE resins are blow molding, extrusion and injection molding. The range of potential end products is quite diverse and includes:</p> <ul style="list-style-type: none"> <li>• Bins, pails and crates</li> <li>• Bottles</li> <li>• Piping</li> <li>• Food packaging films</li> <li>• Caps</li> <li>• Trash liners, sacks and carrier bags</li> <li>• Wire and cable sheathing</li> <li>• Insulation</li> <li>• Surface coating for paper and cardboard</li> </ul>
Ethylene Dichloride/Vinyl Chloride/Polyvinyl Chloride	14	<p>Ethylene is used in the production of ethylene dichloride, which is used to make vinyl chloride monomer (VCM). VCM is polymerized to produce polyvinyl chloride (PVC). PVC applications include:</p> <ul style="list-style-type: none"> <li>• Building and construction (pipe, tile, and flooring)</li> <li>• Packaging (film and bottles)</li> </ul>
Ethylene Oxide (EO)	12	<p>EO is used to produce many derivative products including:</p> <ul style="list-style-type: none"> <li>• Ethylene glycol (intermediate in production of terephthalate polyester resins for fibers, films, and bottles; used in automotive antifreeze)</li> <li>• Glycol ethers (solvents and intermediates in a variety of applications)</li> <li>• Non-ionic surfactants (detergents)</li> <li>• Ethanolamines</li> </ul> <p>EO is also used directly in the gaseous form as a fumigant and sterilizing agent.</p>
Ethylbenzene/Styrene	7	<p>Styrene is produced using ethylbenzene. Derivatives of styrene monomer are styrene-based polymers used in the manufacture of plastics and rubber products such as toys, construction pipe, foam, boats, latex paints, tires, luggage, food-grade film, and furniture. These polymers include:</p> <ul style="list-style-type: none"> <li>• Polystyrene and Expandable Polystyrene</li> <li>• Styrene-Butadiene rubber</li> <li>• Acrylonitrile-Butadiene-Styrene</li> <li>• Styrene-Acrylonitrile</li> <li>• Unsaturated polyester resins</li> <li>• Styrene-butadiene latices</li> </ul>
Linear Olefins	3	<ul style="list-style-type: none"> <li>• Used as base materials for the manufacture of detergents, plasticizers, synthetic lubricants, and additives</li> <li>• Comonomers in the production of polyethylenes</li> </ul>
Others	7	<p>Other chemical manufacturing processes using ethylene include:</p> <ul style="list-style-type: none"> <li>• Ethanol</li> <li>• Ethylene dibromide</li> <li>• Acetaldehyde</li> <li>• Vinyl acetate</li> <li>• Propionaldehyde</li> <li>• Ethyl chloride</li> <li>• Ethylene-propylene elastomers</li> </ul> <p>Ethylene is also used in the controlled ripening of fruit, vegetables, and flowers.</p>

Source: American Chemistry Council<sup>14</sup>

<sup>14</sup> Ibid., 14.

## B. GHG Emissions from Petrochemical Plants – Types and Relevance

### 1. General Considerations

A typical petrochemical plant includes three types of energy consumption, namely: a) fuel consumption – about 60%, b) steam energy consumption – 35%, and c) the remaining 5% – power consumption.<sup>15</sup> With respect to fuel consumption, fuel (naphtha, ethane, LPG, etc.) is combusted directly while emitting carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O).

In this section, we will assess the types and relative amounts of GHGs emitted by the petrochemical industry. In doing so, we will also take into account the Global Warming Potential (GWP) of those gases, namely, the relative quantification of the heat trapped in the atmosphere by each type of GHG.

The most widely known and major GHGs are shown depicted in Table 3, where CO<sub>2</sub> is taken as the baseline and reference gas with a GWP of 1, and the other GHGs are ranked in increasing order based on their relative GWP.<sup>16,17</sup>

**Table 3: Global Warming Potentials (100-Year Time Horizon)<sup>17,18</sup>**

Gas	GWP Gas	GWP
CO <sub>2</sub> .....	1	HFC-227ea..... 2,900
CH <sub>4</sub> * .....	21	HFC-236fa..... 6,300
N <sub>2</sub> O.....	310	HFC-4310mee..... 1,300
HFC-23 .....	11,700	CF <sub>4</sub> ..... 6,500
HFC-32 .....	650	C <sub>2</sub> F <sub>6</sub> ..... 9,200
HFC-125.....	2,800	C <sub>4</sub> F <sub>10</sub> ..... 7,000
HFC-134a.....	1,300	C <sub>6</sub> F <sub>14</sub> ..... 7,400
HFC-143a.....	3,800	SF <sub>6</sub> ..... 23,900
	HFC-152a.....	140

\* The methane GWP includes both the direct effects and the indirect effects of the production of tropospheric ozone and stratospheric water vapor. The indirect effect due to the production of CO<sub>2</sub> is not included.

GWP = global warming potential; CO<sub>2</sub> = carbon dioxide; CH<sub>4</sub> = methane; N<sub>2</sub>O = nitrous oxide; HFC = hydrofluorocarbon; CF<sub>4</sub> = tetrafluoromethane; C<sub>2</sub>F<sub>6</sub> = hexafluoroethane; C<sub>4</sub>F<sub>10</sub> = perfluorobutane; C<sub>6</sub>F<sub>14</sub> = perfluorohexane or tetradecafluorohexane; SF<sub>6</sub> = sulfur hexafluoride.

Source: IPCC 1996. (IPCC=Intergovernmental Panel on Climate Change)

<sup>15</sup> Consultative Group of Experts on National Communications from Parties not included in Annex I to the Convention. *Handbook on Energy Sector, Fuel Combustion*. United Framework Convention on Climate Change.

<sup>16</sup> Saxena, A.K. 2009. *Greenhouse Gas Emissions – Estimation and Reduction*. Asian Productivity Organization, <http://www.apo-tokyo.org/publications/files/gp-19-gge.pdf>.

<sup>17</sup> Climate Action Report. 2010. *Greenhouse Gas Inventory*, U.S. [http://unfccc.int/resource/docs/natc/usa\\_nc5.pdf](http://unfccc.int/resource/docs/natc/usa_nc5.pdf)

## 2. GHG Emissions from Petrochemical Plants – Relative Magnitude and Inventory

### a) IEA GHG Emissions Report

The IEA evaluated the global emissions from oil refining and petrochemicals.<sup>18</sup> This is depicted in Table 4.

**Table 4: GHG Emission Data for Oil Refining and Petrochemicals**

	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub> O
Refineries	686.9 Mt/yr in 1994	5-45 kt/yr in 1994	1-6 kt/yr
Petrochemicals	520 Mt/yr in 1996	Not estimated	150-600 kt/yr (adipic acid manufacture)

Source: Gale et al.<sup>19</sup>

From the reported data, one can make the following observations:

- CO<sub>2</sub> emissions are many orders of magnitude higher than CH<sub>4</sub> emissions, namely, the latter represent less than 1% of CO<sub>2</sub> emissions. Even if one took into account the GWP weighing factors for CH<sub>4</sub>, CH<sub>4</sub> emissions still would represent less than 1% of total GHGs.
- Likewise, CO<sub>2</sub> emissions are much larger than N<sub>2</sub>O emissions even though the latter are higher than what would be expected, especially if one took into account N<sub>2</sub>O's GWP weighing factor. This is mainly caused by adipic acid manufacture. It should be noted, however, that adipic acid manufacture is not included in the primary petrochemical products of focus in the present project. If one did not take the adipic acid manufacture into account, N<sub>2</sub>O emissions would be expected to be much lower than the value reported.

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<sup>18</sup> Gale, J. and Freud, P. *Greenhouse Gas Abatement in Energy Intensity Industries*. IEA Greenhouse Gas R&D Programme, Cheltenham, GL52 7RZ, UK <http://www.ccs101.ca/assets/Documents/ghgt5.pdf>.

<sup>19</sup> Ibid.

## b) ExxonMobil Chemical GHG Emission Estimates

Among the petrochemical companies, ExxonMobil Chemical reported its permit application for the company's proposed Mont Belvieu Plastics Plant in Texas, along with the plant's GHG emission estimations, to the EPA's Federal Implementation Plan (FIP).<sup>20</sup> This facility is a new addition to the existing polyethylene plant at the site. Construction of the new addition would begin in March 2013.

The GHG estimations reported by ExxonMobil Chemical are shown in Table 5. The data suggest that the new plant would emit CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O gases. However, CO<sub>2</sub> emissions amount to about 99% of the total CO<sub>2</sub>e emissions for the proposed project (CO<sub>2</sub>e = CO<sub>2</sub> equivalent). Therefore, the reported estimations suggest that GHG emissions other than CO<sub>2</sub> are negligible by comparison.

**Table 5: ExxonMobil Polyethylene Plant in Mont Belvieu, TX – GHG Emissions**

Air Contaminant Data					
Emission Point			Component or Air Contaminant Name	GHG Emission Rate (tons/yr)	CO <sub>2</sub> e Emission Rate (ton/yr)
EPN	FIN	Name			
RUF61	RUF61	Incinerator	CO <sub>2</sub>	118,497	118,497
			N <sub>2</sub> O	1	310
			CH <sub>4</sub>	2	42
RUPK71	RUPK71	Regenerative Thermal Oxidizer	CO <sub>2</sub>	1,972	1,972
			N <sub>2</sub> O	1	310
			CH <sub>4</sub>	1	21
PEXANALZ	PEXANALZ	Analyzers	CO <sub>2</sub>	11	11
RUFLARE61	RUFLARE61	Low Profile Flare	CO <sub>2</sub>	41,903	41,903
			N <sub>2</sub> O	2	620
			CH <sub>4</sub>	4	84
RUPK31/32	RUPK31/32	Boiler 31/32	CO <sub>2</sub>	33,614	33,614
			N <sub>2</sub> O	1	310
			CH <sub>4</sub>	1	21
PEXFUGEM	PEXFUGEM	Fugitives	CO <sub>2</sub>	2	2
			CH <sub>4</sub>	17	357
PEXENGINE	PEXENGINE	MSS Engine	CO <sub>2</sub>	7	7
			N <sub>2</sub> O	1	310
			CH <sub>4</sub>	1	21
Proposed Project Compliance Total			CO <sub>2</sub>	196,006	196,006
			N <sub>2</sub> O	6	1,860
			CH <sub>4</sub>	26	546
			Total	196,038	198,412

<sup>A</sup> Air contaminant emission rates are contributions to the project CO<sub>2</sub>e compliance total.

Source: ExxonMobil Chemical, GHG Permit Application<sup>21</sup>

<sup>20</sup> ExxonMobil Chemical, GHG Permit Application, Mont Belvieu Plastics Plant, May 2012, <http://www.epa.gov/earth1r6/6pd/air/pd-r/ghg/exxonmobil-mont-belvieu-app.pdf>.

<sup>21</sup> Ibid.

### **c) Chevron Phillips Chemical GHG Emission Estimates**

Chevron Phillips Chemical reported its GHG emission inventory from the Cedar Bayou Plant (Baytown, Texas), which produces various petrochemicals.<sup>22</sup>

The Greenhouse Gas Emissions Summary reported by Chevron Phillips Chemical shows that the plant's eight ethylene steam crackers release about 206,000 tons/year of CO<sub>2</sub> and 94,000 tons/year of CO<sub>2</sub> for natural gas and fuel gas feedstocks, respectively. Actual estimates are shown in Table 6. In addition, CH<sub>4</sub> and N<sub>2</sub>O emissions are 1.2 tons/year and 0.2 tons/year, respectively.

These data are estimates based on the plant's normal operation for all of the steam crackers with maximum hourly firing rate. The aforementioned estimates of GHG emissions imply that CO<sub>2</sub> emissions are overwhelmingly larger than those of CH<sub>4</sub> and N<sub>2</sub>O. CO<sub>2</sub> emissions are much larger by many orders of magnitude than those of CH<sub>4</sub> and N<sub>2</sub>O—even if the GWP weighing factors are taken into account.

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<sup>22</sup> Chevron Phillips Chemical Company LP, Cedar Bayou Plant, New Ethylene Unit 1594, Greenhouse Gas PSD Permit Application, December 2011, [http://www.epa.gov/earth1r6/6pd/air/pd-r/ghg/chevron\\_cedarbayou\\_app.pdf](http://www.epa.gov/earth1r6/6pd/air/pd-r/ghg/chevron_cedarbayou_app.pdf).



**Table 6: Chevron Phillips Chemical, Cedar Bayou Plant – GHG Emissions**

Maximum Firing Rate (HHV) (MMBtu/hr)	72% Conversion Firing Rate (HHV) (MMBtu/hr)	Fuel Type	Fuel HHV <sup>1</sup> (Btu/scf)	Fuel Flow		Fuel Carbon Content <sup>1</sup> (kg C/kg fuel)	Fuel MW <sup>1</sup> (kg/kg-mole)	Emission Factors <sup>4</sup> (kg/MMBtu)		Annual Emissions, ton/yr			
				MMscf/hr <sup>2</sup>	MMscf/yr <sup>3</sup>			CH <sub>4</sub>	N <sub>2</sub> O	CO <sub>2</sub> <sup>5</sup>	CH <sub>4</sub> <sup>6</sup>	N <sub>2</sub> O <sup>6</sup>	CO <sub>2</sub> e <sup>7</sup>
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000
500	412	Natural Gas	1,029	0.49	3,508	0.741	16.64	0.0001	0.00001	206,000	0.4	0.04	206,000
		Fuel Gas	470	1.06	7,680	0.512	5.01	0.0003	0.00006	94,000	1.2	0.2	94,000
		Max:								206,000	1.2	0.2	206,000

Source: Chevron Phillips Chemical Company LP, Greenhouse Gas PSD Permit Application

#### **d) BASF FINA Petrochemicals LP GHG Emission Estimates**

In a permit application to the EPA, BASF FINA Petrochemicals LP reported its estimations for a new steam cracking furnace “package unit.”<sup>23</sup> The package unit includes the boilers, cogeneration and burners, ethane import fugitives, furnace fugitives, and furnace decoking. The estimated CH<sub>4</sub> and N<sub>2</sub>O emissions are less than 1% of the total GHG emissions. CO<sub>2</sub> emissions represent more than 99% of the total actual estimations. Details are reported in Table 7.

<sup>23</sup> BASF FINA Petrochemicals LP, Application for Prevention of Significant Deterioration Air Permit, Greenhouse Gas Emissions, Port Arthur, Texas, 2011, [http://www.epa.gov/earth1r6/6pd/air/pd-r/ghg/basf\\_fina\\_lp\\_ghg\\_app.pdf](http://www.epa.gov/earth1r6/6pd/air/pd-r/ghg/basf_fina_lp_ghg_app.pdf).

**Table 7: BASF FINA Petrochemicals LP (Texas Plant) – GHG Emissions**

EPN	Description	Historical Firing Rate* (mmbtu/yr)	CO <sub>2</sub> (tpy)	CH <sub>4</sub> (tpy)	N <sub>2</sub> O (tpy)	Total CO <sub>2</sub> Equivalent (tpy)
N-16	10th Furnace	0.0	0.0	0.0	0.0	0.0
N-24A	Package Boiler B7280	1,223,228.2	71,954.6	1.4	1.3	72,351.6
N-24B	Package Boiler B7290	1,333,583.1	78,446.1	1.5	1.4	78,878.9
N-20A	Cogen Unit 1 Duct Burner	663,023.9	39,001.4	0.7	0.7	39,216.6
N-20B	Cogen Unit 2 Duct Burner	651,806.0	38,341.5	0.7	0.7	38,553.1
<b>Total</b>			<b>227,743.6</b>	<b>4.4</b>	<b>4.2</b>	<b>229,000.2</b>

Source: BASF FINA Petrochemicals LP, Application for Prevention of Significant Deterioration Air Permit, Greenhouse Gas Emissions<sup>24</sup>

### e) British Petroleum GHG Emissions Report

British Petroleum (BP) reported an inventory of the GHG emissions for its worldwide operations—including the Exploration and Production (E&P) division (upstream) and the Refining and Marketing division (downstream)—which encompasses the petrochemical plants.<sup>25</sup>

The BP report states that the CH<sub>4</sub> emissions come almost exclusively from the company's E&P division, which implies that the Refining and Marketing division (petrochemical plants, refined products) does not emit much in the way of CH<sub>4</sub>. Furthermore, it is well known that methane (70% to 90% in natural gas) is emitted from gas wellheads during crude oil extraction and production as well as from natural gas fields. In all of its reporting and inventory of GHG emissions, BP did not mention any N<sub>2</sub>O emissions from its operations, which suggests that they were negligible in comparison with those of CO<sub>2</sub> and CH<sub>4</sub>.

The relevant data are shown in Table 8.

**Table 8: BP, Greenhouse Gas Emissions, Details for 2007**

Million Tonnes	2001	2002	2003	2004	2005	2006	2007
Direct carbon dioxide (CO <sub>2</sub> ) Million tonnes	73.4	76.7	78.5	76.8	73.2	59.3	59.2
Indirect carbon dioxide (CO <sub>2</sub> ) Million tonnes	10.1	11.4	10.4	9.9	13.9	10.1	10.7

<sup>24</sup> Ibid.

<sup>25</sup> British Petroleum (BP), Greenhouse Emissions, Details for 2007, [http://www.bp.com/liveassets/bp\\_internet/globalbp/STAGING/global\\_assets/e\\_s\\_assets/downloads/bp\\_sustainability\\_report\\_2007\\_greenhouse\\_gas\\_emissions.pdf](http://www.bp.com/liveassets/bp_internet/globalbp/STAGING/global_assets/e_s_assets/downloads/bp_sustainability_report_2007_greenhouse_gas_emissions.pdf).

Direct methane (CH <sub>4</sub> ) Million tonnes	0.3	0.3	0.2	0.2	0.23	0.24	0.2
Direct greenhouse gas Million tonnes CO <sub>2</sub> equivalent	80.5	82.4	83.4	81.7	78.0	64.4	63.5

Source: British Petroleum<sup>26</sup>

#### f) Other GHG Emissions Reports

In the development of an inventory of GHG emissions in South Africa, Bignault and Chitiga-Mabugu (1998)<sup>27</sup> reported that, in all of the energy-intensive industries, including the industrial processes and, more specifically, the chemical industry, CO<sub>2</sub> emissions are 3 to 4 orders of magnitude higher than CH<sub>4</sub> emissions and 4 to 5 orders of magnitude higher than N<sub>2</sub>O emissions. Even if one took into account the GWP weighing factors, CH<sub>4</sub> and N<sub>2</sub>O emissions would amount to only a few percentage points of the total GHG emissions, with CO<sub>2</sub> being overwhelmingly the highest GHG emission contributor.

#### Conclusion

All of the aforementioned information reported by petrochemical companies (Exxon, Chevron, BASF, and BP) is consistent across the board—namely, GHG emissions from petrochemical plants are over 99% composed of CO<sub>2</sub>.

The typical chemical analysis of the process gas suggests that only a very minor amount of CO<sub>2</sub> (parts per million (ppm) order of magnitude) is present in the ethylene tower overhead and the ethylene product.<sup>28</sup> Therefore, the chemical analysis suggests that CO<sub>2</sub> emissions from the process gas/product output of the cracker (inside battery limit [ISBL]) are relatively negligible.

This review of the various sources of CO<sub>2</sub> emissions, as depicted in points a) through f) above, suggests that the flue gas (combustion gas) used to heat the cracker furnaces is the main source of CO<sub>2</sub> emissions. This conclusion is of paramount importance in that almost all of the CO<sub>2</sub>

<sup>26</sup> Ibid.

<sup>27</sup> Bignault, J.N. and Chitiga-Mabugu, M.R. 1998. *Constructing a Greenhouse Gas Emissions Database using Energy Balances, The case of South Africa*, <http://premonline.nl/archive/3/doc/PREM%20WP%2005-03.pdf>.

<sup>28</sup> Siemens Energy & Automation, Inc. *Composition Measurement in Ethylene Plants*, [http://www.sea.siemens.com/us/internet-dms/ia/AppliedAutomation/AppliedAutomation/docs\\_ap/Ethylene.pdf](http://www.sea.siemens.com/us/internet-dms/ia/AppliedAutomation/AppliedAutomation/docs_ap/Ethylene.pdf).

emissions come from the fuel used to “fire” the cracker furnaces. As will be discussed later, most of the power used for the components of the cracker (other than the furnaces) comes from the gas/steam turbo-compressors (CHP) and the third-party supplier of grid power. Any GHG emissions by the grid power supplier at its own site falls out of the scope of this project.

## **C. Petrochemicals in LAC**

### **1. General Observations**

From a production point of view, the LAC petrochemical market includes primarily Brazil, Mexico, Argentina, Colombia, Venezuela, and Chile as well as contributing countries of the Caribbean (such as Trinidad and Tobago) and Central America.

The LAC petrochemical industry has been affected by the global economic recession of 2008. However, some LAC countries suffered less than Western countries such as the United States and the countries in Western Europe did because of their more conservative (or non-existent) lending practices. Brazil, Chile, Colombia, and Peru fared better than other countries in the LAC region during the crisis. Economic recovery in these countries started earlier and continued until the recent fiscal and financial turmoil hit the Southern European countries.

From a global perspective, one may expect the LAC region to be one of the most active investment areas for petrochemical projects behind the Middle East and Asia. This rationale is based upon the average economic growth rate in LAC, which has been higher than in Western countries, but lower than in South East Asia. The Middle East is characterized by new plants that take advantage of a low-cost feedstock (ethane) and proximity to high-demand markets, such as China and India. The latter should remain high-demand markets for many years to come.

### **2. LAC Petrochemical Value Chain**

The flow chart in Figure 3 depicts the petrochemical value chain for the major LAC countries:

**Figure 3: Status of LAC Petrochemical Value Chain**

	Oil & Gas	1 Phase C2 and C3	2nd Phase PE & PP	3rd Phase Processing	4th Phase End Use
Argentina	→	→	→	→	→
Bolivia	→			→	→
Brasil	→	→	→	→	→
Chile	→	→	→	→	→
Perú	→			→	→
Colombia	→	→	→	→	→
Venezuela	→	→	→	→	→
Trinidad & Tobago	→			→	→
México	→	→	→	→	→

Espesor de las flechas refleja la fortaleza relativa

Fuente: Gas Energy, Polyolefins Consulting

Source: Vidal<sup>29</sup>

Where the five value chain steps are as follows:

1. Oil and gas exploration and production, and crude oil refining
2. 1st Phase for petrochemical refining and steam cracking that lead to ethylene (C<sub>2</sub>) and propylene (C<sub>3</sub>) primary chemicals
3. 2nd Phase for synthesis and polymerization to PE and PP
4. 3rd Phase for blow molding, extrusion molding, and injection molding of HDPE, LDPE, and LLDPE
5. 4th Phase for consumer grade products

Figure 3 suggests the following:

a) Brazil and Mexico:

These two countries have a fully integrated petrochemical industry with important crude oil/gas reserves, refining capacities, steam cracking capabilities, adequate conversion into polyethylene and polypropylene, additional processing of other derivatives, and a healthy consumer-products market. In addition, Figure 3 suggests a dominant position for Brazil in almost every aspect of the value chain.

<sup>29</sup> Buhler Vidal, J.O. June 2012. "Situación de la petroquímica regional." Buenos Aires: Reunión Latinoamericana de Logística, 12 de Juno, 2012, <http://www.slideshare.net/buhlerjo/situacion-de-la-petroquimica-regional-61212>.

b) Argentina, Colombia, Venezuela, and Chile:

These four countries have some “weaknesses” in one or more of the five value chain steps. In particular, one may note that the value chains for Venezuela and Argentina are somewhat “diametrically opposed” in that Argentina’s value chain gets progressively stronger from refining to consumer products, whereas Venezuela’s gets “weaker” in the same direction.

c) Peru, Bolivia, and Trinidad and Tobago (T&T):

These countries do not have a fully integrated refining and petrochemical industry. Each one of them is missing some steps in the value chain—mostly in the ethylene steam cracking and PE/PP processing. Figure 3 indicates that T&T has a strong upstream oil and gas sector since the country contains the majority of the Caribbean’s oil production, with a strong export market of natural gas liquids (NGLs) and methanol.

### 3. LAC Petrochemical Supply/Demand Situation

Just before the economic recession of 2007 onwards, LAC’s primary petrochemical production reached a peak of 22 million MT and 20 million MT in 2006 and 2007, respectively, which was helped by strong methanol and benzene exports and higher local demand of ethylene. As the financial crisis and global recession hit the United States and the Western European economies in 2007, LAC’s petrochemical production slowed because of weakening exports and reduced local demand. By 2009, the markets recovered somewhat in the wake of increased exports and rising local demand. Latin American production of primary petrochemicals<sup>30</sup> from 1995 through 2010 is depicted in Figure 4.

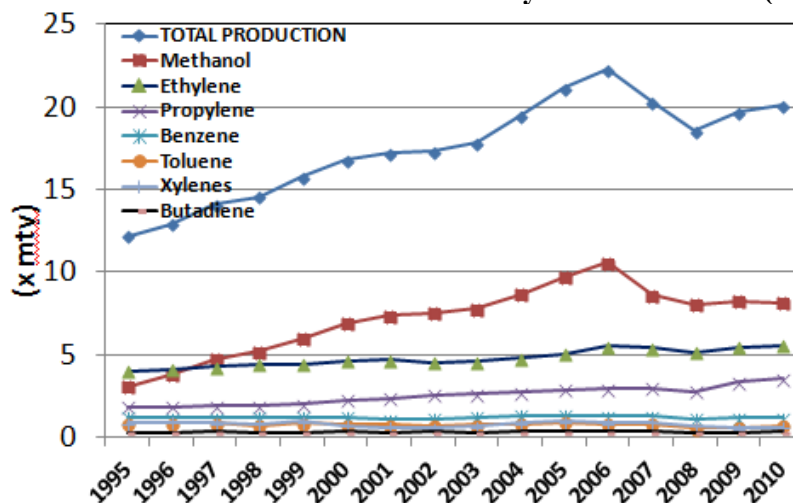
In Figure 4, one may notice that the 2008 recession and reduced demand worldwide hit the total production of all of the primary petrochemicals in Latin America. In addition, the full-year data for 2009 show that total production resumed and increased further in 2010. The 2009 recovery touched on almost all of the petrochemical products, especially propylene, toluene, and

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<sup>30</sup> Davis, S. 2011. “Petrochemical Industry Overview.” *Chemical Economics Handbook*—SRI Consulting, <http://www.scribd.com/doc/77863137/Petrochemical-Industry-Overview>.

ethylene. Furthermore, it is apparent that methanol is, by far, the largest petrochemical product output in LAC.

**Figure 4: Latin American Production of Primary Petrochemicals (x kT)**



Source: SRI Consulting<sup>24</sup>

The production of xylenes never recovered following the higher levels seen in the 2005-2007 timeframe. The plant choices and options of making xylenes and/or aromatics, such as toluene/benzene, constitute a business decision that depends upon the supply-demand situation. From a country perspective,<sup>31</sup> national capacity in ethylene was as follows as of January 1, 2011.

**Table 9: Ethylene Capacity in LAC, January 1, 2011 (x1 mty)**

Brazil	Mexico	Argentina	Venezuela	Colombia	Chile
3.5	1.4	0.84	0.6	0.1	0.05

Source: *Oil & Gas Journal*<sup>32</sup>

Trinidad and Tobago, Chile, Venezuela, Argentina, and Brazil were reported to have the largest methanol capacity in the 2008-2009 time frame in LAC.<sup>33</sup>

The supply-demand scenario for primary petrochemical products is shown in Table 10, which suggests the following observations:

<sup>31</sup> 2010. "Global Ethylene Producers Add Record Capacity in 2010," *International Petroleum and Technology New*, <http://www.ogj.com/articles/print/volume-109/issue-27/special-report-ethylene-reprot/global-ethylene-producers-add-record.html>.

<sup>32</sup> Ibid.

<sup>33</sup> Wongtschowski, P. November 2009. "Ultra, Petrochemical Scenario in Latin America," APLA, [http://www.apla.com.ar/socios/conf29/Presentacion\\_06.pdf](http://www.apla.com.ar/socios/conf29/Presentacion_06.pdf).

- a) With increasing capacity in, and related exports of, methanol from the Middle East, methanol exports from LAC to Western Europe will likely be reduced, the net effect of which will be lower operating output in LAC. From a global perspective, the Latin American methanol production was in the 10% to 15% range in 2010.
- b) The second most widely exported product in LAC, benzene, ships primarily from “long markets,” such as Mexico and Brazil, to “short markets,” such as the United States, Argentina, and Guatemala.
- c) Latin America is a net importer of other petrochemical products—most notably propylene and butadiene.
- d) In view of the current economic climate, i.e., the significant slowdown in the U.S. and the recession in some European countries, it is very hard to postulate an economic forecast for the future in LAC.

**Table 10: Latin American Net Exports of Primary Petrochemicals (x kT)**

	Methanol	Ethylene	Propylene	Butadiene	Benzene	Toluene	Xylenes
1995	639	109	-139	-114	174	17	-41
1996	1,042	116	-263	-119	260	4	-94
1997	2,963	29	-260	-108	264	-7	6
1998	3,778	2	-270	-74	311	-20	11
1999	4,466	28	-233	-124	376	8	-6
2000	5,293	88	-103	-154	281	-27	7
2001	5,819	99	-6	-125	178	21	-12
2002	6,094	129	-72	-146	215	23	-9
2003	5,929	122	-113	-143	315	39	10
2004	7,026	84	-138	-172	285	17	12
2005	8,274	168	-54	-171	428	58	-12
2006	9,198	100	-23	-141	244	52	11
2007	7,338	-66	-112	-175	288	25	12
2008	6,630	58	-204	-173	268	-11	-18
2009	6,980	28	-107	-79	240	-11	-12
2010	6,369	-23	-166	-120	272	5	-14

SOURCE: CEH estimates in conjunction with the World Petrochemicals Program, SRI Consulting.

#### 4. Major Petrochemical Projects in LAC

With abundant crude oil and natural gas reserves, along with more sound investments, LAC should be able to develop and implement major petrochemical projects.



Various petrochemical activities have been undertaken in the LAC region to keep up with increasing demand for polymer and plastic products. This rising demand is spurred by population growth and by a rising standard of living in many LAC countries. This is especially the case in Brazil, Mexico, Chile, Argentina, Colombia, and Trinidad and Tobago. However, the main driver of this petrochemical activity remains Brazil, which accounts for about 50% of related products consumed in the region. Two of the largest petrochemical companies in LAC, namely, Braskem S.A. and Petrobras, are Brazilian entities. These companies also have sizable investments in other LAC countries, such as Mexico, Argentina, and Chile.

One major development that may impact the LAC petrochemical industry is the U.S. shale gas boom (produced by fracking = hydraulic fracturing with horizontal drilling). The resulting low prices of natural gas are encouraging a wave of new and expansions of ethane-fed crackers on the U.S. Gulf Coast.<sup>34</sup>

This new activity is especially detrimental to many Latin American naphtha cracker projects, which are becoming less competitive. This situation is causing some LAC petrochemical companies to suspend (or review) their naphtha cracking projects.<sup>35</sup> The new fracking technology is definitely a game-changer.

Nonetheless, two of the noteworthy petrochemical projects on the books in LAC are as follows:

1) Etileno XX1 Project in Mexico

This petrochemical project is being considered for financing jointly by multilateral and commercial banks. The IDB is considering a loan of US\$300 million to a Joint Venture of Brazil's Braskem S.A and Mexico's Grupo Idesa.<sup>36</sup> The purpose of this project is to develop and operate a petrochemical complex that includes one ethane cracker and three polyethylene plants (two HDPE and 1 LDPE) with an annual capacity of approximately 1 mty. The

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<sup>34</sup> Chang, J. February 2012. "US Shale Gas Boom to Lead Petrochemical Bust," ICIS, <http://www.icis.com/blogs/editorscommentary/petrochemicals/>.

<sup>35</sup> June 2012. "Latin American naphtha cracker projects suspended amid increased shale gas production in USA," Plastemart.com.

<sup>36</sup> Inter-American Development Bank (IDB). April 5, 2012. "IDB to boost competitiveness of Mexico's petrochemical sector," <http://www.iadb.org/en/news/news-releases/2012-04-05/mexico-etileno-xx1-petrochemical-complex,9939.html>.

complex's output will be utilized to manufacture various consumer plastics. PEMEX will supply ethane as feedstock for the plant. Ethane cracker technology is licensed from Technip. HDPE technology is from INEOS, while LDPE technology is licensed from LyondellBasell.<sup>37,38</sup>

The plant will be built at the Coatzacoalcos petrochemical complex in Veracruz, Mexico, and is planned for startup in 2015. Etileno XXI is expected to reduce CO<sub>2</sub> emissions by about 840,000 MT when compared to naphtha-based production.

## 2) Rio de Janeiro Petrochemical Complex (Comperj), Brazil

In March 2008, Petrobras led a gigantic effort to develop and build the Rio de Janeiro Petrochemical Complex (Comperj), which is slated for completion by 2013 and will process about 150,000 barrels (bbls)/day.<sup>39</sup> The project is expected to produce various petrochemical products and derivatives, such as ethane, propane, benzene, butadiene, styrene, ethylene glycol, polyethylene, and polypropylene.

The Shaw Group reported that it had been awarded the cracker design contract by Petrobras with the understanding that the contractor will supply its ethylene technology, along with its Ultra Selective Conversion furnace equipment, as well as basic engineering and technical services for the 1 mty ethylene plant. In addition, the Shaw Group will supply similar services for the recovery section of a fluid catalytic cracking (FCC) unit. *It should be noted that Stone & Webster (the Shaw Group unit for petrochemical plant design) is being taken over by Technip.* The total petrochemical complex project investment is expected to exceed US\$8.5 billion, ranking the complex as one of the largest industrial/petrochemical projects in the world.

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<sup>37</sup>Etileno XXI, International Finance Company (IFC), May 17, 2012, <http://www.ifc.org/ifcext/spiwebsite1.nsf/ProjectDisplay/ESRS30417>

<sup>38</sup> Lupotech, T. February 2011. "Process selected for 300 KT LDPE plant in Mexico." *Hydrocarbon Processing*, <http://www.hydrocarbonprocessing.com/Article/2771471/Lupotech-T-process-selected-for-300-KT-LDPE-plant-in-Mexico.html>.

<sup>39</sup> Rio de Janeiro Petrochemical Complex (Comperj), Chemicals-Technology.com, 2011, <http://www.chemicals-technology.com/projects/riopetrochem/>.

## **II. Specific GHG-Intensive Industries: Design, Energy Balances, CO<sub>2</sub> Emissions**

### **A. Ethylene and Other Olefins, Aromatics**

#### **1. Introduction**

Most of the U.S. and Western European steam crackers were designed and built more than two decades ago. The more recently engineered plants in the Middle East, China, and Brazil have utilized the latest hardware technology, process efficiency, and value chain fractionation. However, many of the older units have been well maintained, and some of them have been revamped and upgraded. The concept of excellent maintenance and best business practices (Total Quality Management (TQM), ISO 9000 series, ISO 14000 series, 6-Sigma, etc.) at the petrochemical plants in developed countries cannot be overlooked.

In one of the studies on “Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions,” the IEA reports that the regional averages for steam crackers suggest a 30% difference in energy use between the best (East Asia) and worst (North America) regions.<sup>40</sup>

In general, one of the main outputs of the steam cracker is ethylene, the production process of which is very energy intensive because of its high heat of reaction and recovery process.<sup>41,42</sup> Ethylene is a relatively inexpensive product with a high reactivity, leading to many petrochemical derivatives that can be generated by oxidation, oligomerization, alkylation, or chlorination, making it the most common petrochemical intermediate.

The petrochemical steam crackers (see typical data in table 11) use a large amount of steam for their operations. The steam can be generated in the plant boilers and/or cogeneration units, also

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<sup>40</sup> OECD/IEA. 2007. “Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions, In support of the G8 Plan of Action,” [http://www.iea.org/textbase/nppdf/free/2007/tracking\\_emissions.pdf](http://www.iea.org/textbase/nppdf/free/2007/tracking_emissions.pdf).

<sup>41</sup> Bowen, C. December 2006. “Olefin Technology Efficiency, Today/Tomorrow.” Paris: Shaw Stone & Webster, Inc., [http://www.iea.org/work/2006/petrochemicals/Bowen\\_Stone&Webster.pdf](http://www.iea.org/work/2006/petrochemicals/Bowen_Stone&Webster.pdf).

<sup>42</sup> Bowen, C. and Jones, D.F. “Mega-olefin plant design: Reality now “Bigger is better,” when planning future ethylene processing capacity.” Houston: Shaw Energy & Chemicals, <http://www.slideshare.net/eargume/mega-planta-de-etileno-steam-cracking>.

called combined heat and power (CHP) units.<sup>43</sup> The high temperature CHP process units are commonly utilized in petrochemical plants—especially in the newer plants.

**Table 11: Typical Furnace Performance Data**

- 1,000 kT/yr ethylene unit, liquids cracking	
- Investment plant cost ~	US\$1.3 billion
Firing rate (residue fuel gas)	825 Mega Watt
Flue gas rate	1190 t/h
CO <sub>2</sub> emissions	155 t/h (13 % of flue gas)
Excess air	10%

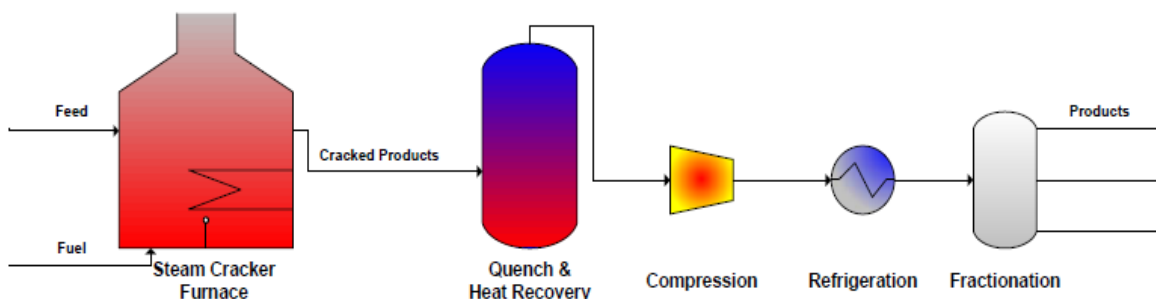
Source: Bowen<sup>44</sup>

It should be pointed out that the various detailed designs and engineering plans of steam crackers created by the hardware suppliers and vendors are proprietary in nature and, thus, kept confidential for obvious reasons. Some cracking furnace emissions data are reported later in this document.

## 2. State-of-the-Art Steam Cracker Components and Processes

In order to better understand the steam cracker operations, the energy consumption, and the corresponding GHG emissions, one needs a detailed analysis of the steam cracker processes. The various steam cracker components, such as the cracking furnace, quench oil/water, gas compression, cracked gas cooling (CGC), and product fractionation and separation columns, are depicted in Figure 5.<sup>45</sup>

**Figure 5: Steam Cracking to Olefins**



Source: Gandler<sup>46</sup>

<sup>43</sup> Combined Heat and Power (CHP), Freedonia, 2003; Plastics Europe, 2006, Rubber Study, 2006; Industrievereinigung Chemiefaser, 2006.

<sup>44</sup> Ibid., 42.

<sup>45</sup> Gandler, T. May 19-22, 2010. “Steam Cracker Furnace Energy Improvements.” Proceedings from the Thirty-second Industrial Energy Technology Conference, New Orleans, LA.

<sup>46</sup> Ibid.

## Step 1 – Steam Cracker Furnace

In general, more than 10 furnaces are utilized in a single ethylene plant, ranging in capacity from 1 mty to more than 1.5 mty. To simplify matters, most petrochemical engineers simply refer to the steam cracker furnace as the pyrolysis section, which is also sometimes called the pyrolysis furnace or cracking furnace. As will be discussed in detail below, this is the most intensive energy process of the steam cracker. There are other descriptions that complement this summary in more detail.<sup>47,48</sup>

The hydrocarbon feedstock—namely, ethane, naphtha, liquefied petroleum gas (LPG), propane, butane, or a mixture of these—enters the steam cracker furnace, where a series of heat exchangers submit it to high pressure and high temperature steam—namely, in the 750-900C range and up to 1,100C in certain cases. In the “firebox,” the hydrocarbon molecules are vaporized by absorbing excess heat. This process splits and breaks up the feed molecules into other smaller hydrocarbon molecules. This is the main reason why the process is referred to as the “steam cracker” of the feed hydrocarbons.

In the pyrolysis section, molecules are cracked, split, and decomposed from large to small via a free-radical mechanism, such as dehydrogenation of ethane. However, there are many other chemical reactions such as the following:<sup>49</sup>

- Ethane ( $C_2H_6$ )  $\rightarrow$  Ethylene ( $C_2H_4$ )+ $H_2$
- Propane ( $C_3H_8$ )  $\rightarrow$  Ethylene ( $C_2H_4$ )+ $CH_4$
- Propane ( $C_3H_8$ )  $\rightarrow$  Propylene ( $C_3H_6$ )+ $H_2$

and many other chemical reactions of “initiation, propagation, and termination”

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<sup>47</sup> Sulzer Chemtech. “Separation Technology for the Hydrocarbon Processing Industry,” <http://www.sbonnett.com/Catalogos/HYDROCARBON%20PROCESSING%20INDUSTRY.pdf>.

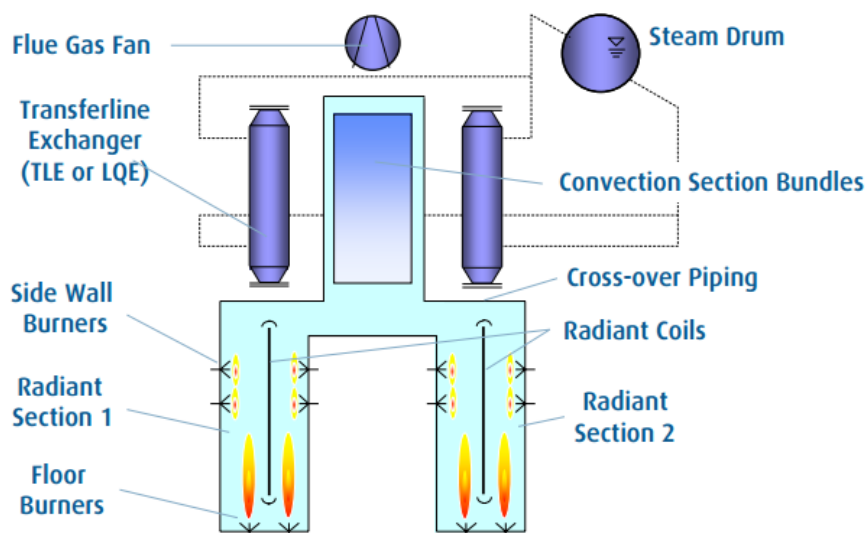
<sup>48</sup> Ren, T., Patel, M. and Blok, K. June 1, 2004. “Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes.” Department of Science, Technology and Society, Faculty of Chemistry, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, The Netherlands, <http://igitur-archive.library.uu.nl/chem/2007-0621-201429/NWS-E-2006-3.pdf>.

<sup>49</sup> Zimmermann, H. and Walzl, R. Ethylene, Hoellriegelskreuth, Federal Republic of Germany [http://media.wiley.com/product\\_data/excerpt/55/35273038/3527303855.pdf](http://media.wiley.com/product_data/excerpt/55/35273038/3527303855.pdf).

The first chemical reaction above, which refers to “ethane cracking” and leads to ethylene and hydrogen, is one of the predominant reactions. Other reactions, such as the splitting of propane molecules into ethylene and propylene (in addition to hydrogen), occur as well. In general, however, other lighter molecules, such as acetylene, methane, propane, butane, etc., are produced as well.

A detailed schematic of the cracker furnace is shown in Figure 6.<sup>50</sup> The figure depicts the energy transfer via radiation (firebox) and convection mostly. The high temperature chemical reactions are endothermic, and heat transfer is achieved via heat exchanger tubular coils. The large feedstock hydrocarbon (HC) molecules are cracked and split into high-value molecules, such as ethylene. In addition, the furnace is a high pressure steam generator and contains low pressure equipment (flue gas and cracked gas).

**Figure 6: Cracking Furnace Set Up and Main Components**



Source: Conrad<sup>51</sup>

One may keep in mind that each furnace module can be as high as 15 stories (50 meters) tall and weigh over 2 kT, the equivalent of the combined take-off weight of five Boeing 747 airplanes.<sup>52</sup>

<sup>50</sup> Conrad, J. 2010. LE Grafik-Büro / 0902 / LE-Präsentation\_D.ppt, Linde AG Engineering Division, Olefin Academy, Munich, <http://olefin-academy.com/documents/Conferenceday2.pdf>.

<sup>51</sup> Ibid.

<sup>52</sup> “World’s Largest Steam-Cracking Furnace Modules Have Arrived at ExxonMobil’s Singapore Petrochemical.” Ordons News Team,

## Step 2 – Quench Tower

The quench tower mostly operates as a partial condenser for the fractionator, and it condenses practically all of the steam and most of the pyrolysis gasoline components. In some designs, the gasoline fractionator and the quench tower are combined into one single structure.

The heat generated by the cracked gas is recovered through the transfer line exchangers (TLEs), which reduce the temperature to the 550-650C range. This is followed by additional cooling to drop the temperature to about 300C while circulating water streams to minimize any further cracking. At this stage, ethylene has been produced but remains mixed with many other hydrocarbons. In addition, this heat is utilized to generate very high pressure steam (up to 125 bars). For ethane crackers (and other gas crackers), cracked gas is cooled to ca. 200C in the TLEs. For naphtha crackers (and other liquid crackers), the process is achieved via quenching oil, which generates low-temperature steam followed by water quenching of the gaseous phase.

The remaining steps will focus on fractionation and separation of the various hydrocarbons. In the quench step, there is a good amount of heat recovered, which is utilized to heat other process steam.

## Step 3 – Gas Compression

In this phase, a centrifugal compressor is utilized to increase the gas fraction pressure to about 3,500 kilopascals (kPas). Subsequent cooling and cleanup are carried out to remove acid gases, carbon dioxide, and water. Most of the dilution steam is condensed and recycled in the system.<sup>53</sup>

The cracked gas, exiting the quench tower, is compressed to allow adequate liquefaction. It must be noted that the cracked gas compressor is the largest power consumer in the process, causing an energy consumption of ~ 0.35 MW/t C<sub>2</sub>H<sub>4</sub>.

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<http://www.ordons.com/asia/southeast-asia/4354-worlds-largest-steam-cracking-furnace-modules-have-arrived-at-exxonmobils-singapore-petrochemical.html>.

<sup>53</sup> Siemens AG . 2007. “Analytics in Ethylene Production Plants, Oil & Gas Industry,” [http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS\\_OG\\_Process\\_Analytics\\_in\\_Ethylene\\_Production\\_Plants.pdf](http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS_OG_Process_Analytics_in_Ethylene_Production_Plants.pdf) Process.

#### Step 4 – Chilling Train or “Cold Section”

The chilling train contains a series of heat exchangers along with refrigeration. The refrigeration phase consists of a series of heat exchangers. One side of the exchangers holds the compressed gas that needs to be cooled, and the other side holds the refrigerant and liquid ethylene, which cool the gas. The compressed gas does not come into direct contact with the liquid phase, which is systematically directed to the distillation towers to separate the various petrochemicals into consumer-grade materials.

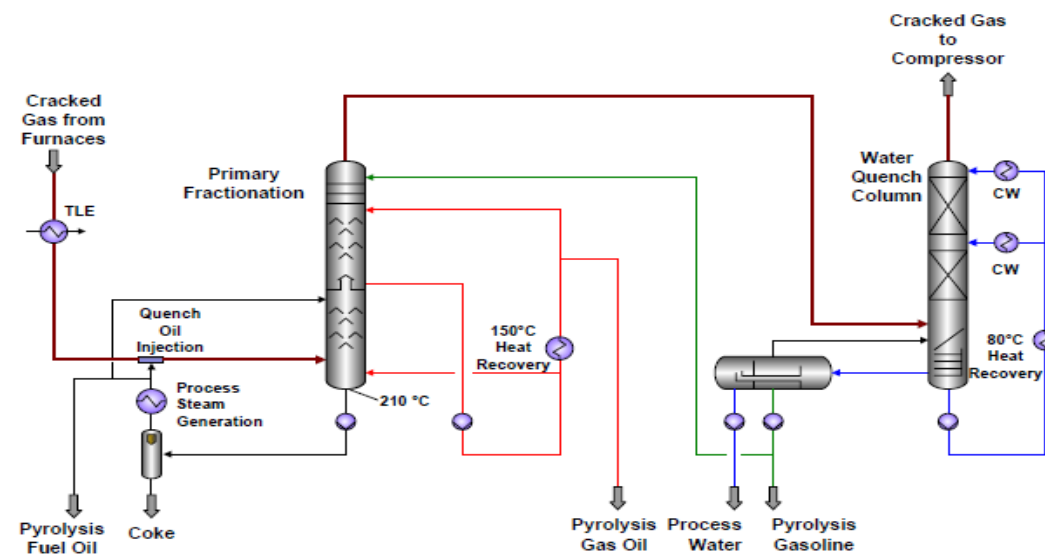
The chilling train condenses most of the heavier hydrocarbons while leaving a rich stream of hydrogen as shown in the aforementioned chemical formula, namely:



#### Step 5 – Fractionation and Separation

A detailed sketch of the fractionation and separation processes is shown in Figure 7.

**Figure 7: Quench Column, Heat Recovery, and Primary Fractionation**



Source: Conradt<sup>54</sup>

The fractionation and separation process is conducted through distillation, refrigeration, and extraction. There are generally three distillation towers, which include the de-methanizer, the

<sup>54</sup> Ibid., 51.



de-ethylenizer, and the de-ethanizer. The de-methanizer separates the other components from the hydrogen and methane, which are used as fuel gas. The remaining heavy gas exits from the bottom of the de-methanizer and is fed into the second distillation tower, called the de-ethylenizer, which separates ethylene from the heavier components in the bottom of the de-methanizer. The third tower, the de-ethanizer, separates ethane from propylene and heavier components in the bottom of the de-ethanizer.

The details of the fractionation towers depend upon the feedstock used, the unit operating conditions, the desired petrochemical product yield, etc. For example, if the feedstock used is propane, one would utilize a distillation tower as a de-propanizer.

In general, steam cracking of ethane (and other gas feedstocks) requires the same first three-step sections that are required for the naphtha cracking process. On the other hand, the detailed processes are somewhat different depending on feedstock characteristics and hardware design, which impact the fractionation and separation sections. For example, ethane cracking operates at a slightly higher temperature in the furnace than naphtha cracking, with a higher capacity of the C<sub>2</sub> splitter but less infrastructure equipment.

Storage tanks and/or recovery equipment for propylene, butadiene, and aromatics are not necessarily needed, but an ethane vaporizer and super-heater are required.<sup>55</sup>

### **3. Steam Cracker Designs, Energy Balances, and GHG Emissions**

The current industry trend in steam cracker design is dictated by feedstock flexibility, finished product quality and yield, relatively low capital expenditure (CAPEX) requirements, high energy efficiency, and GHG emission minimization.<sup>56,57</sup> However, some flexibility and “trade –

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<sup>55</sup> Kantorowicz, S.I. May 2002. “Focus on Profit: C<sub>4</sub> Processing Options to Upgrade Cracker and FCC Streams. ABB Lummus Global. 2<sup>nd</sup> Asian Petrochemical Conference, Seoul, Korea, <http://www.cdtech.com/updates/Publications/Petrochemical%20Papers/C4%20Processing%20Options.pdf>.

<sup>56</sup> Gielen, D., Bennaceur, K. and Tam, C. International Energy Agency – Agence Internationale de l’Energie – 9 Rue de la Fédération – 75015 Paris, [http://www.iea.org/work/2006/petrochemicals/Discussion\\_Paper.pdf](http://www.iea.org/work/2006/petrochemicals/Discussion_Paper.pdf).

<sup>57</sup> Ren, T., Patel, M. and Blok, K. June 2004. “Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes.” Department of Science, Technology and Society, Faculty of Chemistry, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, The Netherlands, <http://igitur-archive.library.uu.nl/chem/2007-0621-201429/NWS-E-2006-3.pdf>.

offs” are sometimes needed between feedstock flexibility and CAPEX requirements, as the two do not necessary come together as will be shown later in more detail.

Most of the major components of cracker designs are similar to the components of ExxonMobil’s steam cracking process, which was developed in the early 1940s. More specifically, the first commercial unit for pyrolysis cracking of hydrocarbons was commissioned at Esso’s facility<sup>58</sup> in Baton Rouge, Louisiana, in 1943. Since then, design upgrades and system refinements have occurred in the five-step process described earlier in this document. However, most of the design improvements have been made for the furnace (pyrolysis) section, which is the most energy-intensive section (60% to 65% of total energy use) and correspondingly the largest GHG emitter in the petrochemical plant.

The first cracking units designed before the 1973 oil crisis suffered from “lack of scale” (small), energy inefficiency, and lack of feedstock flexibility. However, the fourfold increase in crude oil prices after the crisis made energy efficiency a major issue for steam cracker designers and engineers. Since energy efficiency generally comes hand-in-hand with plant scale, namely, the “larger the better,” bigger plants became more prevalent. These are the main reasons that the petrochemical plants were successively “upscaled” to 500 kT/yr in the late 1970s, to 1 mty in the 1980s, and even to 2 mty of ethylene now, the latter being more common in large consumer markets such as the U.S. and the Middle East for exports to China and India. Nonetheless, the average capacity of an ethylene steam cracker around the world today is about 1 mty.<sup>59</sup>

The literature data show significant increases in plant energy efficiencies from 1970 to 2005 as depicted in Table 12. Basically, the data suggest that the plant energy intensity decreased by about half for both ethane and naphtha crackers from 1970 to 2005. In addition, ethane crackers are definitely more fuel efficient than naphtha crackers. This is an intrinsic feedstock feature of ethane crackers, a trend in the petrochemical industry that is driven by abundant and cheap natural gas.

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<sup>58</sup> Kolmetz, K., Kivlen, J., Gray, J. et al. December 14-18, 2002. “Advances in Cracking Furnace Tehcnology.” Refining Technology Conference, Dubai Crown Plaza Hotel, <http://kolmetz.com/pdf/articles/AICFT.pdf>.

<sup>59</sup> Ibid., 42.

**Table 12: Ethylene Plant Efficiencies – Past, Present**

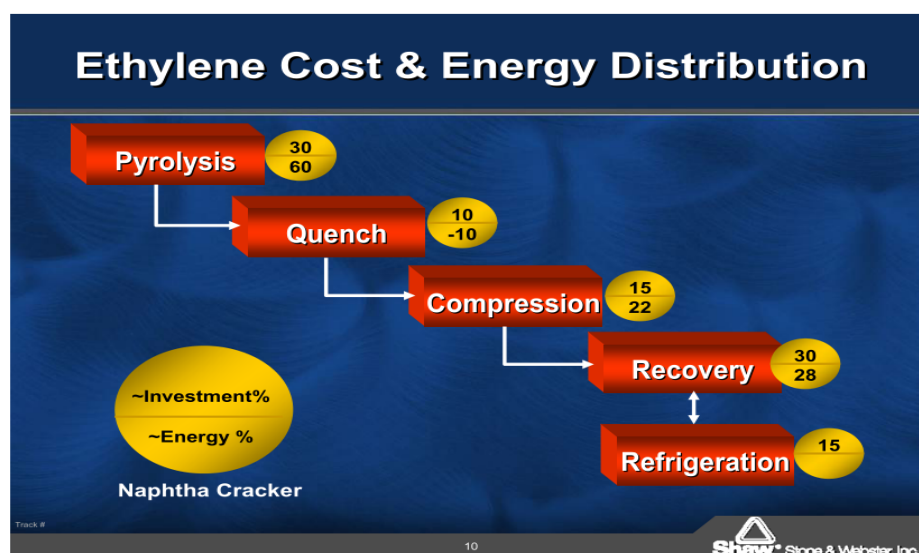
	1970	2005	2011 (added by the writer)
Ethane Crackers, SEC (kcal/kg C <sub>2</sub> H <sub>4</sub> )	~6,600	~3,300	---
Naphtha Crackers, SEC (kcal/kg C <sub>2</sub> H <sub>4</sub> )	~10,000	~5,000	----
Natural Gas Fuel Cost (USGC), US\$/mbtu	~0.2	~5.0	~ 3.0
Imported Crude Oil Cost (USGC) \$/bbl	~6.5	~50	~ 100

Source: Bowen<sup>60</sup>

As pointed out earlier, the energy balance suggests that 60% of the energy comes from the fuel, 35% from the steam, and the remaining 5% from the power grid. It should be noted that, based on these estimates, it may be possible to estimate GHG emissions from the fuel combustion part of the plant, which is one of the main objectives of this study. However, the power grid part of the plant comes from third-party suppliers, who account for their own GHG emissions at power plants.

In terms of the energy balance across the cracker and its main components, in Figure 8, a literature report shows the following details:

**Figure 8: Olefin Technology Efficiency**



Source: Bowden<sup>61</sup>

<sup>60</sup> Ibid., 42.

From the sketch of a naphtha cracker in Figure 8, one can make the following observations:

1. Among the five cracker components, the furnaces (pyrolysis section) consume about 60% of the total system's energy. All other things being equal, this would translate into the highest GHG emissions.
2. The compression and recovery sections account for about 50% of the total energy consumption (while the quench process recovers 10%) and 45% of the total cracker investment. Because these two numbers are relatively high, these two sections do occupy a relatively high priority (after the furnace).
3. On the investment side, the pyrolysis and recovery sections are the most expensive. They are followed by the compression and refrigeration processes.
4. The energy distribution and investment estimates depicted in Figure 8 are for a naphtha cracker. Estimates for an ethane cracker would be lower regarding the total investment as well as the recovery phase (lower slate of products).

In terms of the overall energy consumption of the main components of the cracker, the data shown in Figure 7 and Figure 8 are consistent. In addition, An energy analysis for ethane and naphtha crackers, along with their detailed components, has been published by Ren et al.<sup>62</sup> The specific energy balances across both types of crackers are shown in Table 13.

- The pyrolysis/furnace section consumes 47% of the total energy for the ethane cracker, while the naphtha cracker furnaces consume anywhere from 65% to 73%.
- Detailed data for the naphtha cracker are shown in terms of the percentage of energy used in the compression and separation sections, such as propylene refrigeration (30%), de-ethanizer and C<sub>2</sub> splitter (23%), and fractionation and compression (19%), and the de-methanizer, de-propanizer, and de-butanizer.

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<sup>61</sup> Ibid., 42.

<sup>62</sup> Ren, T. et al. October 21-22, 2004. "Energy Efficiency and Innovative Emerging Technologies for Olefin Production." European Conference on Energy Efficiency, in IPPC-Installations, Vienna, Austria.

**Table 13: Energy/Exergy for Ethane and Naphtha Crackers**

		Ethane	Naphtha				
		Process Energy	Process Energy	Exergy loss			
		[27]	[31]		Our estimate	[26]	[80] [20]
Pyrolysis	Heat of reaction	23%	65%	Fuel combustion and heat transfer to the furnace	75% (or 15 GJ/t ethylene)	73%	N/A
	Steam, heating & losses	24%		Heat exchange with steam, TLEs and heat loss to flue gas		27%	
Fractionation and Compression		22%	15%	Fractionation and Compression	25% (2 GJ/t ethylene in compression and the rest of separation processes)	N/A	19%
Separation		31%	20%	De-methanization			12%
				De-ethanizer and C2 splitter			23%
				C3 splitter			2%
				De-propanization/ De-butanization			10%
				Ethylene refrigeration			5%
				Propylene refrigeration			30%
Total process energy use		100%	100%	Total exergy losses	100% or 17 GJ/t ethylene	100% (only pyrolysis section)	100% (only compression and separation)

Source: Ren et al.<sup>63</sup>

#### 4. Hardware Components and Turbo-Machinery

With regard to the thermal efficiencies of the state-of-the-art cracker units, some data published in the literature suggest the following (see Table 14):

**Table 14: Ethylene Units – Current Key Efficiencies**

• Cracking Furnaces:	Thermal $\eta$ ~94%
• Main Frame Compressors:	Polytropic $\eta$ ~85%
• Main Frame Steam Turbine Drivers:	Isentropic $\eta$ ~80%
• Main Fractionator Towers:	R/D ~1.2 x R/D min
• Principal Heat Exchangers:	Ambient ~10°C LMTD Cryogenic ~ 5°C LMTD
• Major Pumps:	Efficiency ~70%
Turbo-Expanders:	Isentropic $\eta$ ~80%

Source: Bowen<sup>64</sup><sup>63</sup> Ibid.<sup>64</sup> Ibid., 34.

As discussed earlier, appropriate steam crackers are equipped with a CHP system, mainly a steam turbine unit driven by the high temperature and high pressure process gas as it exits from the furnaces. The steam turbine (CHP) system is utilized to drive the other turbo-machines, such as the gas compressor, the ethylene compressor, and the propylene compressor.

A typical world-scale ethylene plant (about 700 mty of ethylene per year) uses a 45,000 horsepower (hp) (34,000 kilowatt [kW]) cracked gas compressor, a 30,000 hp (22,000 kW) propylene compressor, and a 15,000 hp (11,000 kW) ethylene compressor.<sup>65 66</sup>

## **5. Steam Cracker-Specific Energy Consumption and CO<sub>2</sub> Emissions**

As briefly mentioned earlier, there is a direct relationship between the energy intensity of the steam cracker and GHGs—although the relationship is dependent upon parameters such as the types of feedstock, cracker component design and efficiencies, and operating conditions of the olefins' value chains.

Some of the studies on the steam cracker with respect to the SEC have been reported, namely, energy consumed per MT of ethylene (and/or per MT of HVCs), along with specific GHG emissions, namely, CO<sub>2</sub> emitted per MT of ethylene (and/or MT of HVCs).<sup>67,68,69</sup>

In Table 15, the SEC and the specific CO<sub>2</sub> are reported for two typical petrochemical plants, one operating on ethane feedstock and the other on naphtha. It is no surprise that the GHG emissions are reported in terms of CO<sub>2</sub>, which was shown earlier to be the single most important GHG emission compound coming from petrochemical plants.

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<sup>65</sup> Ethylene, Production, Wikipedia.

<sup>66</sup> "Technology Characterization: Steam Turbines." December 2008. Prepared for Environmental Protection Agency, Combined Heat and Power Partnership Program, Washington, DC, Energy and Environmental Analysis, Arlington, VA, 22209, [http://www.epa.gov/chp/documents/catalog\\_chptech\\_steam\\_turbines.pdf](http://www.epa.gov/chp/documents/catalog_chptech_steam_turbines.pdf).

<sup>67</sup> 2000. "Energy and environmental profile of the US chemical industry." Study prepared by Energetics Co. for the Office of Industrial Technology at the U.S. Department of Energy. Columbia, Maryland.

<sup>68</sup> "Petrochemical Processes 2003." *Hydrocarbon Processing*. March 2003. See also [www.hydrocarbonprocessing.com](http://www.hydrocarbonprocessing.com).

<sup>69</sup> Neelis, M., Patel, M. and Feber, M.D. 2003. "Improvement of CO<sub>2</sub> emission estimation from the non-energy use of fossil fuels in The Netherlands." (report nr. NW and S E-2003-10 prepared for NOVEM and VROM) Utrecht, The Netherlands: Utrecht, University.

**Table 15: Specific Energy Consumption and CO<sub>2</sub> Emissions for Olefin Production**

	Ethane	Naphtha
SEC (GJ/t ethylene) <sup>a</sup>	17–21 (typical) and 15–25 (maximum)	26–31 (typical) and 20–40 (maximum)
SEC (GJ/t HVCs)	16–19 (typical)	14–17 (typical)
CO <sub>2</sub> emission (t CO <sub>2</sub> /t ethylene) <sup>b</sup>	1.0–1.2 (typical)	1.8–2.0 (typical)
CO <sub>2</sub> emission (t CO <sub>2</sub> /t HVCs)	1.0–1.2	1.6–1.8
Ethylene yield (wt%) <sup>c</sup>	80–84	29–34 (30% typical)
Propylene yield (wt%)	1–1.6	13–16
Butadiene yield (wt%)	1–1.4	4–5
Aromatics and C4+ yield (wt%)	2–3	10–16
HVCs yield (wt%)	82 (typical)	55 (typical)
Methane yield (not counted as HVCs) (wt%)	4.2	13–14
Hydrogen yield (not counted as HVCs) (wt%)	4.3	1
Backflows to refinery (not counted as HVCs) (wt%)	0	9–10
Losses (due to fouling, coking, etc.) (wt%)	1–2	1–2

Source: Ren et al.<sup>70</sup>

In analyzing the figures regarding the SEC, CO<sub>2</sub>, and HVCs, one may make the following observations:

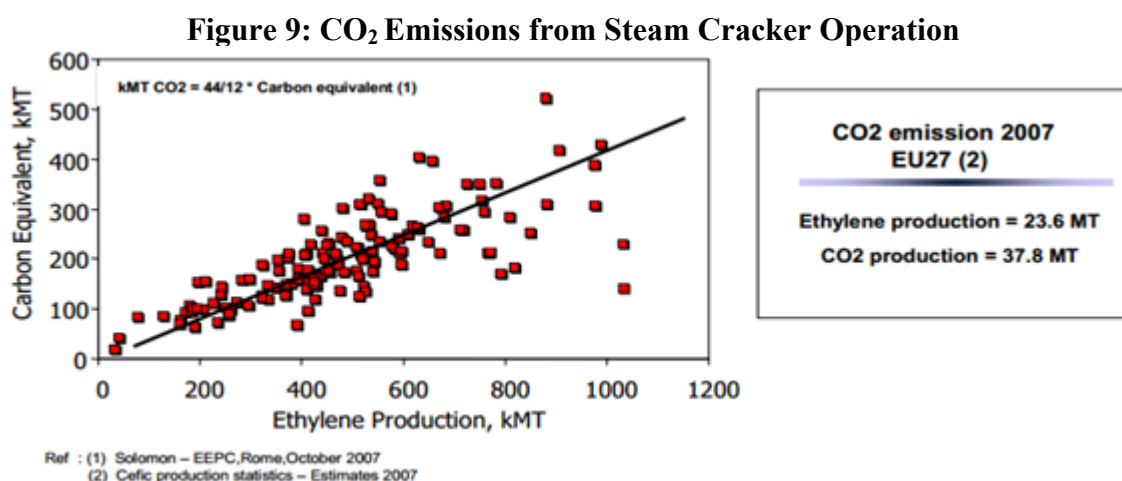
- a) A naphtha cracker is more energy intensive and emits more CO<sub>2</sub> on a relative basis per unit of ethylene produced than an ethane cracker, namely,
  - i. ca. 73% more CO<sub>2</sub>/t ethylene
  - ii. ca. 55% more CO<sub>2</sub>/t HVCs
- b) In terms of the SECs per total HVCs produced, ethane and naphtha crackers are comparable.
- c) For the CO<sub>2</sub> emitted per metric ton of HVCs produced, ethane crackers are better performers than naphtha crackers.
- d) Ethane crackers have the highest yield of ethylene (80% to 84%), while naphtha crackers yield a higher amount of other HVCs, such as propylene, butadiene, and

<sup>70</sup> Ibid., 58.

other aromatics. In addition, naphtha crackers produce significant amounts of other byproduct.

- e) From a benchmark basis, one may notice that, for a state-of-the-art ethane steam cracker, there seems to be a near direct relationship of 1 to 1 between 1MT of CO<sub>2</sub> emitted and 1 MT of ethylene produced.
- f) Likewise, there seems to be a near direct relationship of 1 to 1 between 1MT of CO<sub>2</sub> emitted and 1 MT of HVCs produced by an ethane cracker.

Points e) and f) above may represent preliminary benchmarks for future cracker design, engineering, and construction. These points seem to constitute a generalized benchmark for cracker-specific energy consumption versus CO<sub>2</sub>-specific emissions, which has also been reported by the European Chemical Industry Council for European steam crackers.<sup>71</sup> The original work was published at the European Ethylene Producers Committee Meeting in Rome.<sup>72</sup> The correlative data is shown in Figure 9.



The correlation curve of CO<sub>2</sub> emissions (expressed in kMT) versus ethylene production (kMT) is as follows:

<sup>71</sup> “An allocation method for Petrochemicals.” The European Chemical Industry Council Ad Hoc Group Energy, Feedstock & Logistics, February 8, 2008, CEFIC, Brussels, January 16, 2008, [http://ec.europa.eu/enterprise/sectors/chemicals/files/wg\\_7\\_8fer08/14leuckx\\_sectoral\\_en.pdf](http://ec.europa.eu/enterprise/sectors/chemicals/files/wg_7_8fer08/14leuckx_sectoral_en.pdf).

<sup>72</sup> Solomon Associates LLC, European Ethylene Producers Committee (EEPC), Rome, October 2007.



$\text{kMT CO}_2 = 44/12 * \text{Carbon equivalent}$

The information above indicates that there is a significant correlation between plant efficiencies and CO<sub>2</sub> emissions. (Note: Figure 9 utilizes carbon equivalent, whereas Table 15 shows actual CO<sub>2</sub> emissions per MT of ethylene.) Therefore, any effort by a plant to reduce CO<sub>2</sub> emissions can be done via an increase in the plant's energy efficiency.

In addition, for ethylene production higher than ca.750 kMT/yr, the correlation curve seems to suggest that the plant emits less carbon equivalent on a relative basis. This suggestion makes sense, as the related petrochemical plant becomes more energy efficient with scale and, thus, emits less CO<sub>2</sub> per kMT of ethylene produced. This conclusion was included in the publication "Mega-olefin plant design: Reality now "Bigger is better" when planning future ethylene processing capacity," which was published at the European Ethylene Producers Committee Meeting in Rome in 2007.<sup>73</sup>

## **6. Investment Costs for the Steam Cracker and its Hardware Components**

### **a) Petrochemical Plant Investment versus Capacity**

Various reports published in the petrochemical literature suggest a standard relationship between initial investment cost and plant capacity for most olefin plants.<sup>74</sup> This suggests that the total installed cost (TIC) per MT of ethylene decreases with an increase in plant production, with the exponential factor of investment versus capacity that applies ranging from  $p = 0.77$  to  $0.80$ —this being slightly higher than the usual value of  $0.66$  to  $0.70$  for petrochemical plants due to the effect of compressors and heat exchangers.

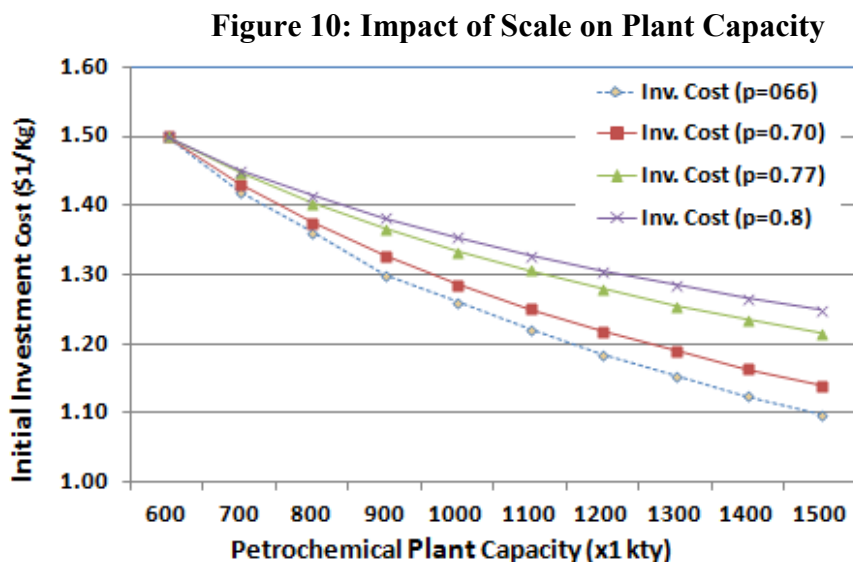
It should be noted, however, that the data reported are based on the latest petrochemical plants built in the U.S., the Middle East, and Asia, which benefit from the latest technologies. For example, the new plants built in the Middle East, mostly ethane-based crackers, are in the high capacity range, namely, 1.5 to 2 million MT/yr.

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<sup>73</sup> Ibid., 42.

<sup>74</sup> Buffenoir, M.H., Aubry, J.M. and Hurstel, X. January 2004. "Large ethylene plants present unique design, construction challenges." *Oil & GS Journal*.

On the basis of the information reported in the literature,<sup>75,76,77,78,79</sup> mill the impact of scale on plant capacity was plotted in Figure 10, with the “reference plant” selected at a US\$900 million investment for 600 kty capacity, which is more representative of a plant in LAC than the aforementioned 1 mty plant is for the U.S. and Western Europe.



The estimates, plotted for various p factors, clearly show that, as the plant capacity is increased, the initial total investment cost decreases on a relative basis. It should be noted that most data in the literature are reported in terms of production costs versus plant capacity.

To illustrate the observations above, a plant investment versus capacity plot is shown in Figure 11.<sup>80</sup> More specifically, the relative decrease in investment cost with increased plant capacity is significant, going from 0.22 US\$/lb @ 500 kT to 0.18 US\$/lb @ 1,500 kT.

<sup>75</sup> “Global ethylene capacity continues advance in 2011.” *Oil & Gas Journal*.

<sup>76</sup> “New Dow ethylene plant would employ thousands,” <http://fuelfix.com/blog/2012/04/19/dow-to-announce-new-houston-area-plant/>.

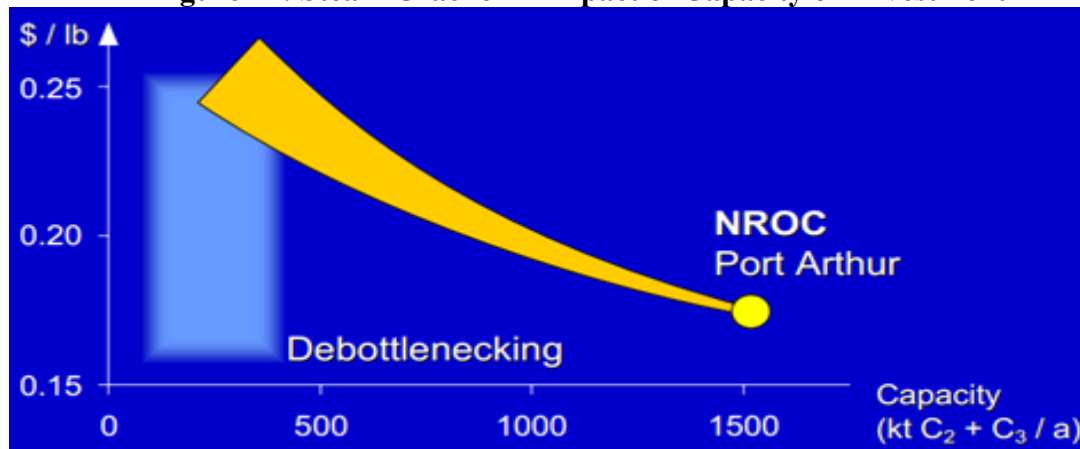
<sup>77</sup> “Dow plans Texas ethylene plant based on shale gas.” *Oil & Gas Journal*, <http://www.ogj.com/articles/print/vol-110/issue-4d/general-interest/dow-plans-texas-ethylene.html>.

<sup>78</sup> “Dow Chemical’s new cracker at Freeport.” Houston (Platts) – April 2012, <http://www.platts.com/RSSFeedDetailedNews/RSSFeed/Petrochemicals/6202631>.

<sup>79</sup> “An Introduction to Industrial Chemistry.” Chapter 6.7.3, *Plant Capital*. 119-121.

<sup>80</sup> Hambrecht, J. June 12, 2001. “Adding value through growth and innovation, Petrochemicals: The Road Ahead.” BASF Aktiengesellschaft, Houston, [http://www.basf.com/group/corporate/en/function/conversions:/publish/content/investor-relations/news-publications/presentations/2001/download/010612\\_hambrecht.pdf](http://www.basf.com/group/corporate/en/function/conversions:/publish/content/investor-relations/news-publications/presentations/2001/download/010612_hambrecht.pdf).

**Figure 11: Steam Cracker – Impact of Capacity on Investment**



Source: Hambrecht<sup>81</sup>

The capacity of the prospective future LAC plant will *likely* fall in the middle of the capacity range, namely, in the 500 kT to 1 million MT capacity because of possible investment ceilings and weak local demand, which might fail to absorb all of the petrochemical production—at least in the near future. Of course, the closeness of the plant to the major consumer market is another factor to be taken into account (to simplify logistics and enhance competitiveness).

b) Plant Component Comparisons and “Upscaling”

Some comparative studies on plant sizes have been reported as they relate to components’ design, dimensions, power requirements, and operating conditions. A comparative study of 600 kty versus 1.4 mty plants is shown in Table 16.

<sup>81</sup> Ibid.

**Table 16: Plant Size Comparison**

Item	Reference, 600,000 tpy	Jam, 1.4 million tpy
Number of furnaces	9 + 1 spare	9 + 1 spare
Transfer line diameter, in.	72	60 and 80
Primary fractionator diameter, <sup>1</sup> m	7 (all heaters)	6.6 (liquid heaters only)
Quench tower diameter, <sup>1</sup> m	6.5	1 at 6.5, 1 at 6.5 and 5.2
Charge gas power, <sup>2</sup> Mw	35	56
Propylene refrigeration, <sup>2</sup> Mw	20	37
Ethylene refrigeration, <sup>2</sup> Mw	5	12
Ethylene fractionator	4-m diameter	6-m diameter, 670 tonnes
Propylene fractionator	4-m diameter	6-m diameter, 700 tonnes
Cold water circulation, <sup>3</sup> 1,000 cu m/hr	35	70
Flare stack	42-in. diameter, 90-m high	64-in. diameter, 160-m high

<sup>1</sup>Reference case uses standard internals, Jam uses high-capacity devices. <sup>2</sup>Mechanical power for the steam turbine driver. <sup>3</sup>Temperature rise = 7° C.

Source: Buffenoir<sup>82</sup>

From the information in Table 16, one can make the following observations:

- When comparing the two different-sized plants, the number of furnaces is about the same (9 + 1 spare); however, the latest designs for liquid-cracking furnaces use symmetrical U-type radiant coils, which have increased capacities by up to 25% within identical radiant firebox dimensions, multi-pass convection, and a variable RPM-induced flue gas fan to optimize combustion conditions during startup/decoke/turn-down, etc.
- The charge gas power has almost doubled from 35 MW to 65 MW, as has ethylene and propylene refrigeration.
- The propylene fractionator diameter has increased by 50%. The flare stack diameter has increased by ca. 50% as well.
- Other “upscale” measures and state-of-the-art designs for larger plants are reported by Bowen et al.<sup>83</sup>

<sup>82</sup> Ibid., 76.

c) Investment Costs Regarding Plant Hardware Components

With regard to the major hardware components utilized in a typical steam cracker, findings on investment costs in the published literature suggest the cost information in Table 17.<sup>84,85</sup>

**Table 17: Investment Cost for Steam Cracker  
Hardware Components**

Equipment	Cost Fraction, %	Exponent
Furnace <sup>62</sup>	30	0.8 – 0.9
Heat Exchangers	21	1
Compressors	31.5	0.7
Vessels	12.6	0.67
Pumps, Other	4.9	0.5
Total	100	

Source: Buffenoir et al.,<sup>86</sup> Heaton et al.<sup>87</sup>

On the basis of the information above, one can make the following comments:

- The furnace investment cost may be underestimated via the calculation based on Ref. 56 because:
  - It is not clear whether the quench section is already included in the definition of “furnaces,” as some refiners and petrochemical engineers include it, while others do not.
  - The delineated cost fractions are assumed to be ISBL—namely, they may not include tank farms, utility equipment, shipping/receiving facilities, building/office space, etc.
- The information in Table 17 can be utilized as guidance for investment benchmarks in future petrochemical (ethane cracker) plant design, construction, and potential funding

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<sup>83</sup> Ibid, 42.

<sup>84</sup> Ibid, 76.

<sup>85</sup> “An Introduction to Industrial Chemistry.” Chapter 6.7.3. *Plant Capital*. 119-121, [http://books.google.com/books?id=sAoXqiukH2IC&pg=PA119&lpg=PA119&dq=ethylene+cracker+furnace+cost&source=bl&ots=NkDg7xu2bn&sig=0773tXqwK\\_f4eZ22DOejK8kvxQA&hl=en&sa=X&ei=s7UAUIj5OYm08ATp3sGUCA&ved=0CHUQ6AEwCDgo#v=onepage&q=ethylene%20cracker%20furnace%20cost&f=false](http://books.google.com/books?id=sAoXqiukH2IC&pg=PA119&lpg=PA119&dq=ethylene+cracker+furnace+cost&source=bl&ots=NkDg7xu2bn&sig=0773tXqwK_f4eZ22DOejK8kvxQA&hl=en&sa=X&ei=s7UAUIj5OYm08ATp3sGUCA&ved=0CHUQ6AEwCDgo#v=onepage&q=ethylene%20cracker%20furnace%20cost&f=false).

<sup>86</sup> Ibid., 76.

<sup>87</sup> Ibid., 87.

considerations. The information indicates that the most investment-intensive components are: a) furnaces, b) compressors, and c) heat exchangers.

- It has been reported that a naphtha cracker can be 30% more expensive than an ethane cracker, mainly for the recovery of various byproducts.

## 7. Steam Cracker Technology Licensors

The steam cracker design and the engineering of a petrochemical plant are typically supplied by a contractor, which includes the five major licensors, namely, the Linde Group, Lummus Global (CBI), Kellogg Brown & Root (KBR), Technip, and Stone & Webster (being purchased by Technip from the Shaw Group). Each one of these licensors offers proprietary technology for ethylene steam cracking with one or more feedstocks as well as yields in primary olefins and derivatives.

These licensors continue to introduce improvements to their process, and, on occasion, they may offer new and innovative process routes. A summary of the main vendors for steam cracker design and technology is shown in Table 18. The data was gathered from reports available in the literature.<sup>88,89</sup>

**Table 18: Steam Cracker Technology Vendors and Licensors**

	<b>Technip S.A.</b>	<b>Lummus Technology Inc.</b>	<b>Linde A.G.</b>	<b>Stone &amp; Webster (being taken over by Technip)</b>	<b>KBR</b>
<b>Pyrolysis (Cracking) Furnace</b>	<ul style="list-style-type: none"> <li>– SMK* gas feed to furnace coil enables very large capacity crackers</li> <li>– GK6* liquid feed enables a 35% increase in production</li> </ul>	Feed preheated and cracked with steam in tubular short residence time (SRT)	PyroCrack furnaces are optimized with residence time, temperature, and pressure profiles for feedstock to achieve high olefin yields	Feeds to ultra selective cracking (USC*) cracking furnaces within the requirements specific to the feedstock and product requirements	<ul style="list-style-type: none"> <li>– KBR combined with ExxonMobil's olefin technology</li> <li>– SCORE pyrolysis features the straight tube SC-1 design, other conditions to produce high olefin yields</li> </ul>
<b>Other Steam Cracker Components (than Furnace)</b>		Single refrigeration system with metathesis to	– Waste heat is recovered to boilers and process heaters	ARS technology for reduced chilling train requirements, reduced methane,	Various flow-schemes based on de-ethanizer-first, de-

<sup>88</sup> Ibid., 63.

<sup>89</sup> Ibid., 81.

	Not available	increase propylene output catalytically with 15% less energy consumed	– Process is optimized with flexibility and long intervals between major turnarounds	partial de-ethanizer bypassing, dual feed ethylene fractionator, and reduced refrigeration demand (ca. 75%)	propanizer-first, and de-methanizer-first configurations
<b>Energy Efficiency and Yield</b>	Not available	– 3,300 kcal/kg for ethane cracking – 5,000 kcal/kg for naphtha cracker	– Ethylene yields are 25%, 35%, 45%, and 83% for gas oils, naphtha, LPG, and ethane, respectively – Specific energy consumption is ca. 6,000/5,400/4,600 and 3,800 kcal/kg of ethylene	– Ethylene yields from 57% (ethane, high conversion) to 28% (heavy gas oils). – Specific energy consumptions range from 3,000 kcal/kg to 6,000 kcal/kg	Ethylene yields up to 84% for ethane, 38% for naphtha, and 32% for gas oils.
<b>Gas Turbine</b>	Not available	3 GJ/t of ethylene saved	Not available	Offered, but no data	Not available
<b>Ethylene Yield, wt%</b>	35%	34.4%	35%	Not available	38%
<b>SEC, GJ/t of Ethylene</b>	18.8 (best) or 21.6 to 25.2 (typical)	18 (with gas turbine) 21 (typical)	21 (best)	20 to 25	No data
<b>Global Installed Capacity and/or Market Share</b>	– Production capacity the last 10 years of 7 mty – 25% the last 10 years	~ 40% of the world's ethylene plants	Over 15 million tons of ethylene produced in more than 40 plants worldwide	– Over 120 ethylene units built – Expansion techniques based on ARS technology have increased original capacities by over 100%	Collaborated in over 140 ethylene projects with capacities up to 1.3 mty since 1990

\*SKM, GK6 and USC are registered trademarks

Source: Ren et al.,<sup>90</sup> *Hydrocarbon Processing*<sup>91</sup>

Overall, the reported information in Table 18 suggests that the competing vendors have comparable technologies, as this is a very mature industry.

From the information in Table 18, one may make the following observations:

- One of the main descriptive points relates to the specific design of the pyrolysis furnace to enhance energy efficiency and reduce emissions.
- The other point of differentiation is the design and operating conditions of the fractionation/separation sections, such as the de-methanizer, de-ethanizer, and de-

<sup>90</sup> Ibid., 63.

<sup>91</sup> “Petrochemical Processes 2003 (Ethylene - Phenol).” March 1, 2003. *Hydrocarbon Processing*.

propanizer—especially the order in which they are used to improve energy efficiency and HVC yield.

- The SECs (GJ/metric ton of ethylene) are in the range of 18 to 25 for all of the competitors; the differences are not significant enough to draw conclusions.
- The ethylene yields are also comparable in the range of 34% to 38%—which suggests that the compared technologies are for naphtha crackers (relatively low yield in ethylene).
- Some of the vendors indicate the use of gas/steam turbines (powered by the process steam via a CHP system), which would reduce the grid power consumption for the cracker operation and the compressors used in the downstream phases (gas compression, ethylene/propylene refrigeration, etc.).
- One may make the assumption that all technology licensors would now supply the CHP turbo-compressor system, an essential feature from a competitive point of view. In any case, CHP is one of the major energy efficiency improvements of the steam cracker, which reduces GHG emissions.
- The data for ABB Lummus (now a CBI company) for the steam turbine suggest an ethylene saving of 3 GJ/t. If one compares this saving with the total energy used in the cracking process shown in Table 18, one comes up with a 15% to 20% energy efficiency improvement for naphtha cracking.

An informative discussion about state-of-the-art steam cracking technology is provided in the literature.<sup>92</sup>

## **8. Feedstock Impact on Energy Efficiency, CO<sub>2</sub> Emissions, and Yield**

From the early 1970s until the last decade, naphtha steam cracking was the preferred process for the production of primary petrochemicals and their derivatives. Over the last few years, however, ethane cracking has made a dramatic push in the petrochemical industry. How and

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<sup>92</sup> “Downstream focus: Lummus Technology.” February 2010. *Arabian Oil & Gas*, <http://www.arabianoilandgas.com/article-6909-downstream-focus-lummus-technology/>



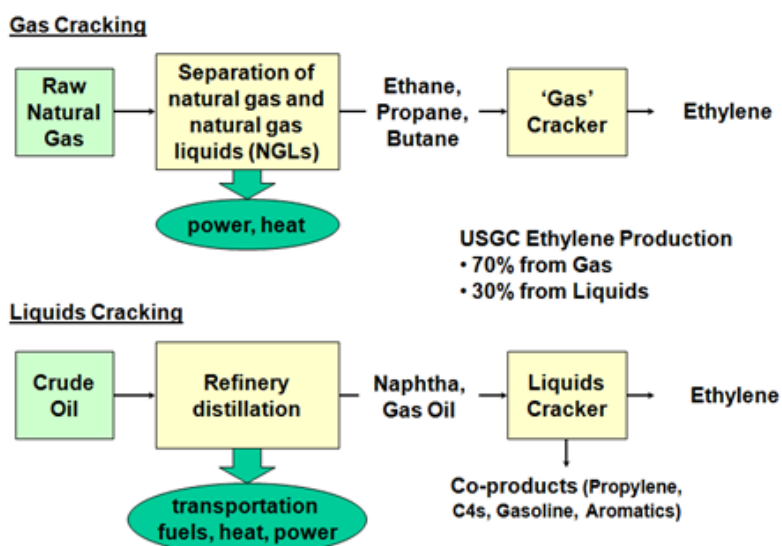
why did this happen? There are many reasons for this industry trend toward gas crackers—especially ethane-fed pyrolysis furnaces. This will be discussed thoroughly later in this document.

#### a. Process Complexity and the Investment Cost of Liquid Crackers versus Gas Crackers

Gas crackers (such as those that are ethane-fed) are generally less complex than liquid-fed crackers because of the production of fewer by-products—especially  $C_3$  petrochemicals such as propylene. The complexity of liquid-fed crackers (such as naphtha crackers) comes with a higher investment cost—up to 30% higher—when compared to the cost of an ethane-fed cracker for the same HVC nominal capacity.

On the other hand, the main advantage of liquid-fed crackers over those that are gas-fed is in the yield of propylene, butadiene, and other aromatics—at the expense of a lower yield of ethylene. From a flow process point of view, the respective value chains for each type of cracker are shown in Figure 12.<sup>93</sup>

**Figure 12: Petrochemical Feedstock – Oil and Gas**



Source: Keeth<sup>94</sup>

<sup>93</sup> Keeth, F. "Is Liquids Cracking the Future of Gulf Coast Petrochemicals," <http://www.bauer.uh.edu/centers/uhgemi/documents/Fran%20Keeth%20GEMI%20Conference%20pres%20%20v042505.ppt>.

<sup>94</sup> Ibid.

As can be seen in the flow chart in Figure 12, the main output of gas crackers is ethylene (up to 80% output), with the other two principal by-products being hydrogen and methane, which are often separated and recycled as fuel. On the other hand, liquid crackers produce much higher amounts of C<sub>3</sub> and C<sub>4</sub> derivatives. The main conclusion is that a trade-off may have to be made between more C<sub>3</sub>/C<sub>4</sub> derivatives with a higher plant investment and fewer C<sub>3</sub>/C<sub>4</sub> derivatives and a lower plant investment.

#### **b. Influence of Feedstock on Steam Cracker Efficiency and CO<sub>2</sub> Emissions**

In referring to Table 18 and more specifically to the line item labeled “Energy Efficiency & Yield,” one may notice that the data reported by Lummus Technology, Inc., Linde AG, and Stone & Webster are pretty consistent: the naphtha cracker consumes almost twice the amount of relative energy (expressed in Kcal/Kg) than the ethane cracker does in ethylene production.

Another important consideration is the carbon intensity of the feedstock—namely, the lower the carbon intensity of the feedstock, the lower the overall CO<sub>2</sub> emissions in the total value chain, as some of the feedstock is recycled as fuel gas to the cracker.

Table 19 depicts the various types of fuel. It is not surprising that ethane is the most favorable feedstock, and it has the lowest CO<sub>2</sub> emission factors.

**Table 19: Intrinsic CO<sub>2</sub> Emission Factors for Various Feedstocks**

Feedstock Type	CO <sub>2</sub> Emission Factor (Per Unit Energy), kg CO <sub>2</sub> /MMBtu	CO <sub>2</sub> Emission Factor (Per Unit Mass or Volume), kg CO <sub>2</sub> /MMBtu
LPG (average for fuel use)	63.16	5.79
Propane	63.07	5.74
Ethane	59.58	4.14
Naphtha (< 401 F)	66.51	8.31

Source: Greenhouse Gas Emission Guidelines<sup>95</sup>

In this discussion about feedstock, the focus is on plant economics, energy efficiency, and CO<sub>2</sub> emissions. The feedstock availability factor, landed pricing at the plant, and product quality are

<sup>95</sup> “Greenhouse Gas Emission Guidelines: Stationary Combustion Sources.” April 2009, [http://daq.state.nc.us/monitor/eminv/forms/Stationary\\_Combustion\\_Sources.pdf](http://daq.state.nc.us/monitor/eminv/forms/Stationary_Combustion_Sources.pdf).

other parameters that need to be considered. However, these parameters fall outside of the scope of the current project.

## B. Polyethylene and Polypropylene

### 1. General Considerations

Polyethylene (PE) is derived from the main olefin output of a petrochemical plant, namely, ethylene, via various polymerization schemes. PE is a tough, semi-crystalline material; it has numerous commercial applications (as described in Table 2); and it has the highest production volume of any plastic.<sup>96</sup>

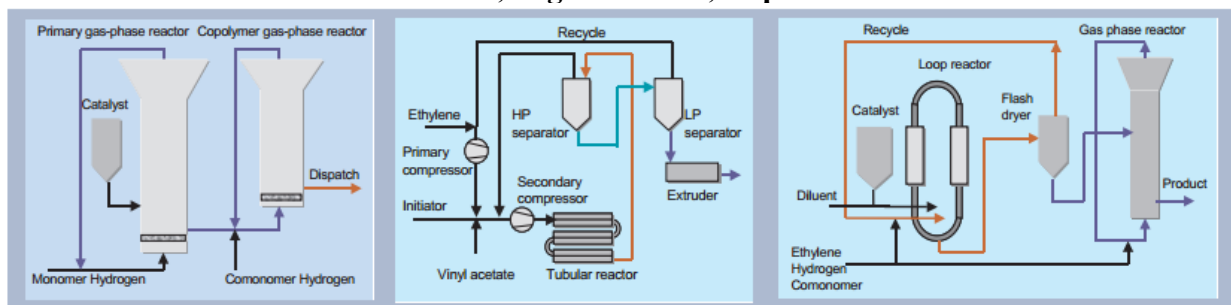
### 2. Manufacturing Processes

There are many manufacturing processes, depending upon the desired product specifications, density, and end use. In general, there are two broad categories of PE manufacturing processes, namely:

- a. Low pressure processes
- b. High pressure processes

The PE manufacturing categories are depicted in the flow diagrams in Figure 13.

**Figure 13: PE Production Processes (left to right)  
– Gas Phase, High Pressure, Liquid Phase**



Source: Siemens<sup>97</sup>

<sup>96</sup> “Global HDPE/MDPE, Markets, Technologies & Trends.” Chemical Market Resources, Inc., <http://cmrhoutex.com/media/mcs/Prospectus%20for%20PR1114%20-%20Global%20HDPE%20MDPE%20Markets%20Technologies%20and%20Trends.pdf>.

<sup>97</sup> “Process Analytics in Polyethylene (PE) Plants.” 2007. Case Study. Siemens USA.

### Low Pressure Processes

The low pressure processes are utilized to manufacture three types of PE, namely, LLDPE, MDPE, and HDPE. These PE chemicals are produced in a coordinated polymerization scheme via a catalyst at low pressure (10 to 80 bars) and a temperature ranging from 70 to 300 C. These low pressure processes are carried out in either a gas-phase or liquid-phase polymerization scheme as follows:

#### a) Gas-Phase Polymerization<sup>98</sup>

In this manufacturing process, ethylene is in contact with a solid catalyst in an agitated bed of dry polymer powder. The gas-phase polymerization technology is generally economical; it can utilize a wide range of catalysts. It is the most widely utilized manufacturing process in *state-of-the-art-plants that convert ethylene to PE*.

#### b) Liquid-Phase Polymerization<sup>99</sup>

In suspension processes, the catalyst and polymer particles are suspended in a hydrocarbon (such as propane). In slurry processes, ethylene polymerization occurs with a boiling solvent in stirred tank reactors. A wide range of catalysts is used in this liquid-phase polymerization process.

### High Pressure Processes

On the other hand, a high pressure process (>3,000 bars and a temperature of 300°F to 575°F) is used to produce the more conventional LDPE, which is carried out either in an autoclave or a tubular process.

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[http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS\\_Process\\_Analytics\\_in\\_PE\\_Plants.pdf](http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS_Process_Analytics_in_PE_Plants.pdf).

<sup>98</sup> Anderson, K. April 7, 2006. "Polyethylene R&D." The Dow Chemical Company, Freeport, Texas, Invited Lecture for Chem 470 – Industrial Chemistry, Texas A&M University.

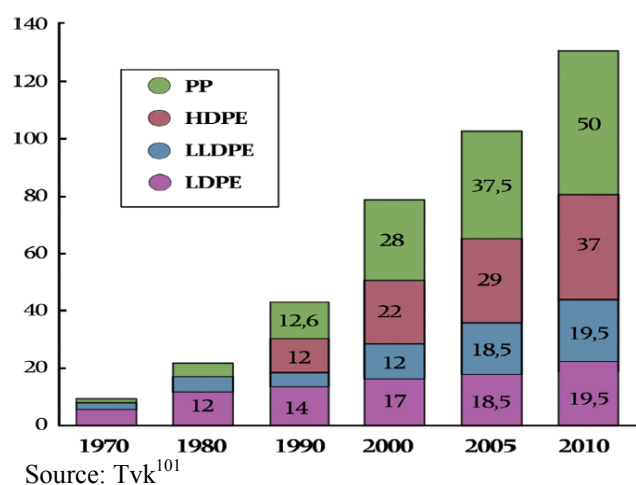
<sup>99</sup> Ibid.

With an organic peroxide, the chemical reaction generates free radicals, the process of which leads to the formation of both long and short branches by “side” reactions<sup>4</sup> but not in a linear mechanism.<sup>100</sup>

### 3. Production of Polyethylene and Polypropylene

Polyethylene and polypropylene (PP) are the largest-volume petrochemicals produced in the world. The global growth rate of various types of PE and PP is shown in the chart in Figure 14.

**Figure 14: PE and PP Global Growth from 1970 through 2010**



The chart in Figure 14 suggests that there has been a good annual increase of all of the four product grades, especially PP, HDPE, and LLDPE, over the last 10 years.

### 4. Some Observations on the Various PE Chemicals

The various PE chemicals used in commercial applications are as follows:

- a) LDPE, which has a random and long chemical branching, is a translucent solid that is characterized by lower tensile strength (“weak” intermolecular forces) and increased ductility. LDPE is mostly used in blown film.<sup>102</sup>

<sup>100</sup> “Status of Low Pressure PE Process Licensing,” <http://www.scribd.com/doc/76297471/Status-of-Low-Pressure-Polyethylene-LDPE-Process-Technology-Licensing-CMR-Inc-Analysis>.

<sup>101</sup> OLEFINS PRODUCTION, “Olefins by steam cracking,” [www.tvk.hu/repository/713326.pdf](http://www.tvk.hu/repository/713326.pdf)

<sup>102</sup> Ibid., 46.

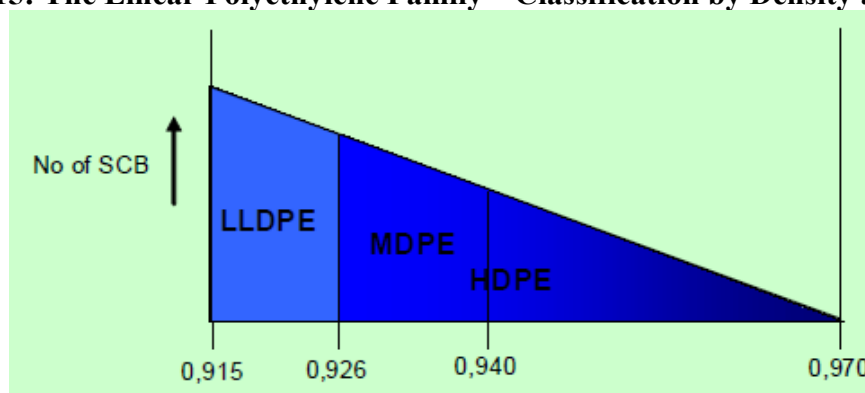
b) LLDPE, a substantially linear polymer, with significant numbers of short branches and longer-chain olefins, is also a translucent solid.<sup>103</sup> It is generally utilized in wire and cable coatings, bubble wrap, and piping.

c) MDPE, which has a high degree of resistance to chemicals, has a good hardness to durability ratio and can be spread in a thin layer for plastic sheeting to use in packaging. It is utilized in a wide range of plastic sheeting, tubing, and plastic fittings.<sup>104</sup>

d) HDPE consists of very straight chains of ethylene with a much narrower distribution of molecular weights and a very high average chain length. Because of its very high density and wide chemical distribution, it is utilized in various commercial applications, such as plastic bottles, caps, containers, film, pipes, etc.

Figure 15 depicts the classification by density and short chain branching (SCB)

**Figure 15: The Linear Polyethylene Family – Classification by Density and SCB**



Source: Csaba<sup>105</sup>

## 5. Technology Licensors

### a) Low Pressure Technologies

The low pressure processes for manufacturing LLDPE, MDPE, and HDPE are as follows: a) liquid phase (slurry and solution), and b) gas phase.

<sup>103</sup> Lyondell, <http://www.lyondellbasell.com/Technology/LicensedTechnologies/Spherilene/>.

<sup>104</sup> ChemSystems, [http://www.chemsystems.com/about/cs/news/items/PERP%200809\\_1\\_LDPE.cfm](http://www.chemsystems.com/about/cs/news/items/PERP%200809_1_LDPE.cfm).

<sup>105</sup> Csaba, A. 2010. "HDPE Technology Including MDPE and LLDPE."

The well-known licensors for low pressure technologies are depicted as follows for each production process:<sup>106</sup>

#### Liquid Phase

##### Slurry Process

- Phillips Slurry Loop (Licensor: Chevron Phillips Chemical)
- Solvay Loop (Licensor: Solvay)
- Hostalen (Licensor: Basell)
- Nissan (Licensor: Nissan) in joint efforts of Nissan, Maruzen, and Equista
- CX Process (Licensor: Mitsui)

##### Solution

- Dowlex (Proprietary: Dow)
- Sclairtech/AST (Licensor: NOVA)
- Compact (Licensor: Stamicarbon-SABIC)

#### Gas Phase

- Unipol (Licensor: Univation)
- Innovene (Licensor: BP Amoco)
- Spherilene (Licensor: Basell)

#### b) High Pressure Technologies

The two basic technologies for manufacturing LDPE, together with the related technology licensors, are as follows:<sup>107</sup>

##### i. Tubular Process Technologies and Licensors

There are several companies that license LDPE technology based on the tubular process, including differences in the tubular reactor systems used and pressure control mechanisms. The best-known technology licensors are ExxonMobil, LyondellBasell, and SABTEC.

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<sup>106</sup> Ibid., 100.

<sup>107</sup> Ibid., 106.

ii. Autoclave Processes

There are also several companies that license autoclave processes, including ExxonMobil, ICI/Simon Carves, LyondellBasell, and Polimeri Europa (EniChem).

## 6. Energy Intensity of Polyethylene and Polypropylene Manufacturing Processes

In a 2006 study, Schyns<sup>108</sup> published some energy intensity data on the European plants, based on the Weighted EU Average and Best Practice as shown in Table 20.

**Table 20: Energy Intensity in PE and PP Manufacturing Processes**

	Weighted EU Average (GJ/MT)	EU Best Practice (GJ/MT)
LDPE High Pressure Process (Tube and Batch Reactors)	8.53	5.96
HDPE Low Pressure Process (Suspension and Gas-Phase Processes)	5.43	3.14
Polypropylene (Suspension and Gas-Phase Processes)	3.56	2.27

Source: Schyns<sup>109</sup>

The data in Table 20 suggest the following:

- The energy intensity for manufacturing LDPE is almost twice as high as it is for HDPE.
- The energy intensity for the production of HDPE is higher than it is for polypropylene.
- The 2006 EU Best Practice suggests an energy intensity that is around 30% lower than that actually used, on average, in European plants.

When referring to Table 15 for information on the production of ethylene and other HVCs, one may note that the energy intensity of PE/PP production is much lower than that for any HVC.

<sup>108</sup> Schyns. December 2006. "Feedstock Substitutes, Energy Efficiency Technologies and CO<sub>2</sub> Reductions in Petrochemical Products." Presentation at the IEA/CEFIC Workshop Feedstock Substitutes. Paris, France.

<sup>109</sup> Ibid.



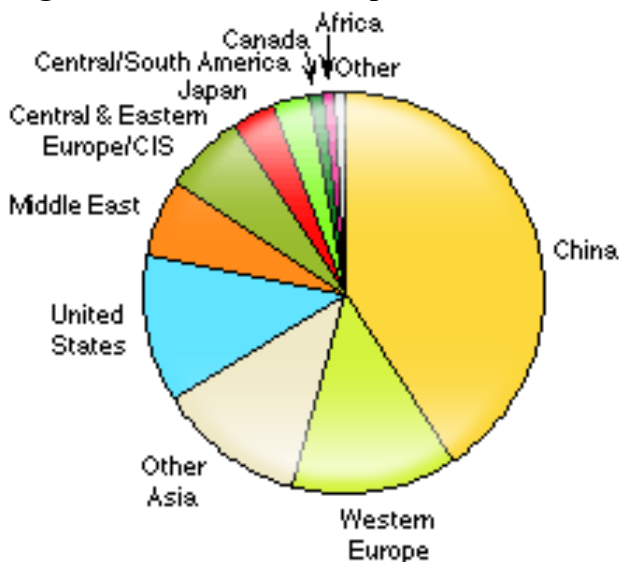
## C. Methanol

### 1. Some Observations on Methanol

Methanol is generally made from natural gas as well as coal, depending upon availability and cost. It can be utilized in various commercial applications, such as antifreeze and solvents, and, most notably, as transportation fuel to reduce tail pipe emissions. It is less toxic than gasoline and diesel, and it is considered biodegradable.<sup>110</sup> In terms of the 2006 global derivatives production, 19% is used to make methyl tertiary butyl ether (MTBE), a gasoline additive; 10% is used for acetic acid; and 40% is used for formaldehyde. About 80% of world production is from natural gas, while the rest comes from coal (mainly in China).<sup>111</sup>

The Latin American methanol production was ca. 7 million MT in 2010; this is depicted in Figure 4. On a global basis, the chart in Figure 16 shows the South/Central American consumption of methanol.<sup>112</sup>

**Figure 16: World Consumption of Methanol (2010)**



Source: IHS<sup>113</sup>

<sup>110</sup> Bonneville Power Administration, P.O. Box 3621, Portland, OR 97208-3621, [http://www.bpa.gov/energy/n/tech/fuel\\_cell/methanol.cfm](http://www.bpa.gov/energy/n/tech/fuel_cell/methanol.cfm)

<sup>111</sup> Ibid.

<sup>112</sup> IHS Chemical, 2010, <http://www.ihs.com/products/chemical/planning/ceh/methanol.aspx>.

<sup>113</sup> Ibid.

The two most widely used methods of producing methanol are either high-pressure or low-pressure synthesis gas processes.<sup>114</sup> In the latter processes, the chemical reaction utilizes a copper catalyst at a pressure of 50 to 100 bars and a temperature of 250°C.

## 2. Energy Intensity of Methanol Plants

A typical methanol plant uses about 30 GJ of natural gas energy to produce 1 MT of methanol. The theoretical minimum energy use (close to Best Applicable Technology) is about 20 GJ/t, which is about 30% lower than the average plant's energy consumption.<sup>115</sup>

In 2006, Lurgi GmbH<sup>116</sup> reported that the large-scale, autothermal reforming plants operate with an energy use as low as 28.5 GJ/t.

Allard<sup>117</sup> reported that the overall efficiency of the conversion of biomass to methanol is 50% to 60%, assuming a gasification efficiency of 80%, while, for natural gas conversion to methanol (the baseline case), the overall efficiency is 64% to 72%.

## 3. Methanol Chemical Processes

Methanol can be produced from a very wide range of feedstocks, namely, natural gas, coal, biomass, agricultural and timber waste, solid municipal waste, and other feedstocks.<sup>118</sup> This unique feature makes it one of the most flexible chemical commodities.

The typical manufacturing process for methanol requires two steps. First, one needs to convert natural gas into a stream composed of CO, CO<sub>2</sub>, H<sub>2</sub>O, and hydrogen, which is followed by catalytic reforming of feed gas and steam. Second, one needs to catalytically synthesize methanol from the synthesis gas.

This overall process can be summarized via the following chemical reactions:<sup>119</sup>

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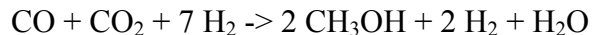
<sup>114</sup> Ibid., 115.

<sup>115</sup> International Energy Agency. 2007. *Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions*. ENERGY, INDICATORS, © OECD/IEA, [http://www.iea.org/textbase/nppdf/free/2007/tracking\\_emissions.pdf](http://www.iea.org/textbase/nppdf/free/2007/tracking_emissions.pdf).

<sup>116</sup> Lurgi. 2006. "Lurgi Mega Methanol," [http://www.lurgi.com/website/fileadmin/pdfs/brochures/Br\\_MegaMethanol.pdf](http://www.lurgi.com/website/fileadmin/pdfs/brochures/Br_MegaMethanol.pdf).

<sup>117</sup> Allard, M. "Issues associated with widespread utilization of methanol." SAE Paper No. 2000-01-0005.

<sup>118</sup> The Methanol Institute (MI) - <http://www.methanol.org/Methanol-Basics/Overview/How-is-Methanol-Made.aspx>.



#### 4. Methanol Production Technology

In the production of methanol, natural gas is heated, desulfurized, mixed with steam, and fed into the synthesis gas reactor. Synthesis gas is subsequently cooled and compressed to an appropriate pressure to allow for methanol synthesis in a series of reactors. The crude methanol is fed into a methanol distillation section, where it is stabilized and prepared for transport.<sup>120</sup>

In general, the three plant process sections may be considered separate modules for design purposes; the related technologies may be selected and optimized separately for each module. The relevant criteria for the selection and use of technology are generally CAPEX, plant efficiency, and product specifications. From an investment point of view, the synthesis gas preparation/compression generally accounts for about 60% of the investment. Almost all of the energy is consumed in this initial process section.<sup>121</sup>

The aforementioned observations imply that the synthesis gas preparation is, by far, the most important, both in terms of investment and energy intensity. There are basically three reforming technologies for the production of synthesis gas.<sup>122</sup>

- a) **One-step reforming** with fired tubular reforming, where the synthesis gas is prepared by tubular steam reforming (without  $\text{O}_2$ )
- b) **Two-step reforming**, which includes fired tubular reforming (primary reforming) followed by oxygen-fired reforming (secondary reforming)

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<sup>119</sup> Ibid.

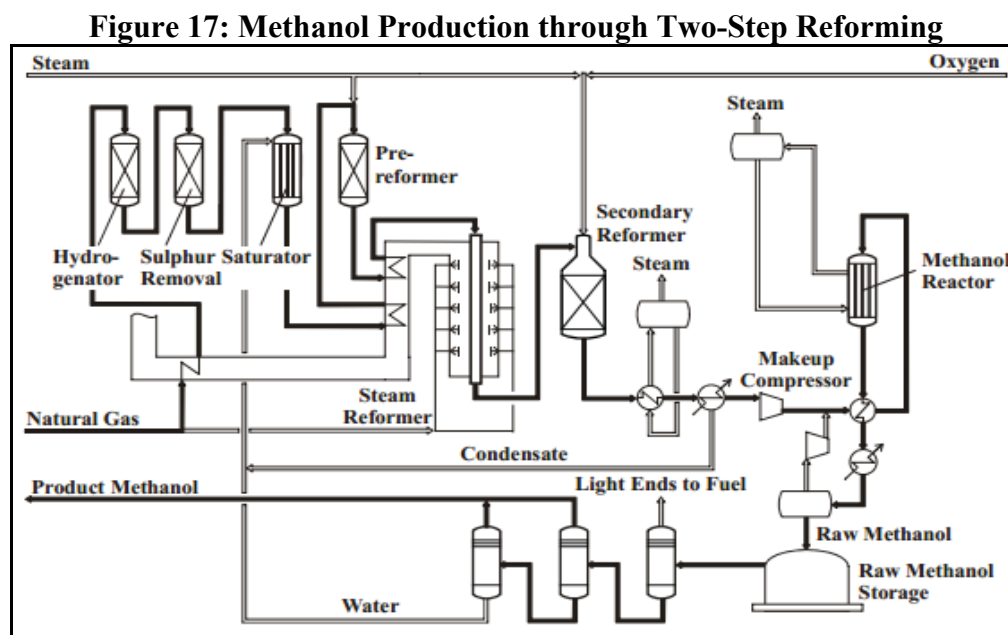
<sup>120</sup> "Process Analytics in Methanol Plants." 2007. Case Study. Siemens AG.  
[http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS\\_Process\\_Analytics\\_in\\_Methanol\\_Plants.pdf](http://www.industry.usa.siemens.com/automation/us/en/process-instrumentation-and-analytics/process-analytics/pa-case-studies/Documents/CS_Process_Analytics_in_Methanol_Plants.pdf)

<sup>121</sup> Aasberg-Petersen, K., Stub Nielsen, C., Dybkjær, I. et al. "Large Scale Methanol Production from Natural Gas." Haldor Topsoe,  
[http://www.topsoe.com/business\\_areas/methanol/~media/PDF%20files/Methanol/Topsoe\\_large\\_scale\\_methanol\\_prod\\_paper.ashx](http://www.topsoe.com/business_areas/methanol/~media/PDF%20files/Methanol/Topsoe_large_scale_methanol_prod_paper.ashx).

<sup>122</sup> Aasberg-Petersen, K., Christensen, T.S., Dybkjær, I. et al. 2007. "Synthesis gas production for FT synthesis." Haldor Topsøe A/S, Nymøllevej 55, Lyngby, Denmark; Sasol Technology R&D, P.O. Box 1, Sasolburg, 1947, South Africa.

- c) **Autothermal reforming (ATR)**, which involves a single oxygen-fired reformer that includes a burner, a combustion section, and a catalyst bed.

A flow diagram of methanol production through two-step reforming, based on a Haldor Topsoe A/S process,<sup>123</sup> is shown in Figure 17.



Source: Aasberg-Petersen<sup>124</sup>

## 5. Technology Contractors and Licensors

There are many technology licensors for methanol plant design and construction. A brief synopsis of the most widely known licensors is provided as follows:<sup>125</sup>

- a) **The Linde Group**, a Germany-based company, utilizes an isothermal reactor, where the catalyst is submerged in a coil-wrapped heat exchanger, which controls the reactor temperature through the generation of steam.

<sup>123</sup> Ibid.

<sup>124</sup> Ibid., 106.

<sup>125</sup> The Linde Group, <http://www.linde-india.com/userfiles/image/File/Synthesis,%20Ammonia%20and%20Methanol%20Plants.pdf>.

- b) **Lurgi GmbH**, a Germany-based company, uses an autothermal reformer for synthesis gas generation and a two-stage synthesis reactor system that consists of a gas-cooled and a water-cooled reactor with very favorable temperature profiles over the catalyst bed.
- c) **ThyssenKrupp Uhde GmbH (Uhde)**, a Germany-based company, utilizes steam reforming for synthesis gas generation and an isothermal tubular reactor with the catalyst contained in vertical tubes providing low by-product formation. Uhde supplies isothermal and adiabatic reactors as well. The isothermal reactor is generally perceived as the most efficient system.
- d) **Haldor Topsoe A/S**, a Denmark-based company, uses a steam reforming system for synthesis gas generation and a straight-tube boiling water reactor for methanol synthesis. The company has another technology that is based on autothermal reforming followed by a boiling water synthesis reactor.
- e) **Davy Process Technology Ltd**, a UK-based company, utilizes two-stage steam reforming that is followed by a synthesis loop, which can operate at pressures between 70 to 100 bars.

## D. Ammonium and Urea

### 1. Background Information and Observations

Ammonia ( $\text{NH}_3$ ) is a stable, colorless gas at ordinary temperatures. It is very soluble in water, and its solubility decreases with increasing temperature. Ammonia can be highly toxic to a wide range of organisms. In humans, the major risk is from inhalation of ammonia vapor, the effects of which include irritation and corrosive damage to the skin, eyes, and respiratory tracts.<sup>126</sup>

Urea ( $\text{NH}_2\text{CONH}_2$ ) is a leading nitrogen fertilizer worldwide. It is a stable, colorless, and odorless solid at room temperature that melts at  $135^\circ\text{C}$ . It is highly water soluble and will

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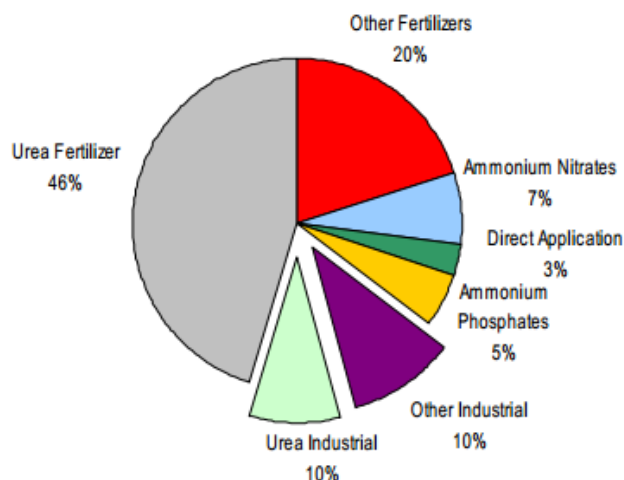
<sup>126</sup> Brigden, K. and Stringer, R. December 2000. *Ammonia and urea production*. Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter, UK, <http://www.greenpeace.to/publications/profertil%20report.pdf>.

slowly hydrolyze in the presence of water to give ammonium carbamate, which slowly decomposes into ammonia and carbon dioxide.<sup>127</sup>

Ammonia is one of the largest chemicals manufactured from hydrocarbons. It is the main element in the value chain for producing fertilizers such as urea fertilizer, ammonium nitrates, ammonium phosphates, and a wide range of industrial applications, such as synthetic resins, polyurethanes, and refrigeration.<sup>128</sup>

In the pie chart in Figure 18, global ammonia consumption is depicted by commercial application.<sup>129</sup> The chart suggests that urea fertilizer is, by far, the largest application—accounting for almost half of the total ammonia derivatives.

**Figure 18: Global Ammonia Consumption  
by Product Application (2010)**



Source: ChemSystems<sup>130</sup>

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<sup>127</sup> Ibid.

<sup>128</sup> *Ammonia and Urea, Strategic Business Analysis*, ChemSystems, 2009/10 Prospectus, [http://www.chemsystems.com/reports/search/docs/prospectus/SBA09\\_Ammonia\\_Urea\\_Prospectus.pdf](http://www.chemsystems.com/reports/search/docs/prospectus/SBA09_Ammonia_Urea_Prospectus.pdf).

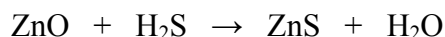
<sup>129</sup> Ibid.

<sup>130</sup> Ibid., 112.

## 2. Chemical Synthesis

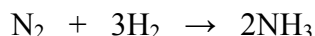
### a. Ammonia Synthesis

Ammonia is synthesized from hydrogen contained in natural gas (main feedstock) and nitrogen contained in air. Natural gas contains some sulfurous compounds, which can damage the catalysts used in this process.<sup>131</sup> These are removed by reacting them with zinc oxide, e.g.,



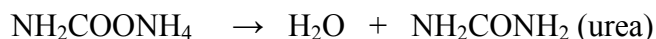
The methane from the natural gas is then converted to hydrogen, and air is mixed with the gas stream to give a hydrogen/nitrogen ratio of 3:1, CO and CO<sub>2</sub>. Carbon monoxide is then converted to carbon dioxide for use in urea production, and the carbon dioxide is removed.

The nitrogen and hydrogen are then reacted at a high temperature and pressure using an iron catalyst to form ammonia:



### b. Urea Synthesis

Urea is synthesized from ammonia and carbon dioxide. The ammonia and carbon dioxide are typically fed into a reactor at a high temperature and pressure, and the urea is manufactured in a two-step process as follows:<sup>132</sup>



The resulting urea contains un-reacted NH<sub>3</sub> and CO<sub>2</sub> and ammonium carbamate. As the pressure is reduced and heat is applied, the NH<sub>2</sub>COONH<sub>4</sub> decomposes into NH<sub>3</sub> and CO<sub>2</sub>. The ammonia and carbon dioxide are then recycled. The urea solution is then concentrated to give 99.6% w/w molten urea and granulated for use as fertilizer and chemical feedstock.<sup>133</sup>

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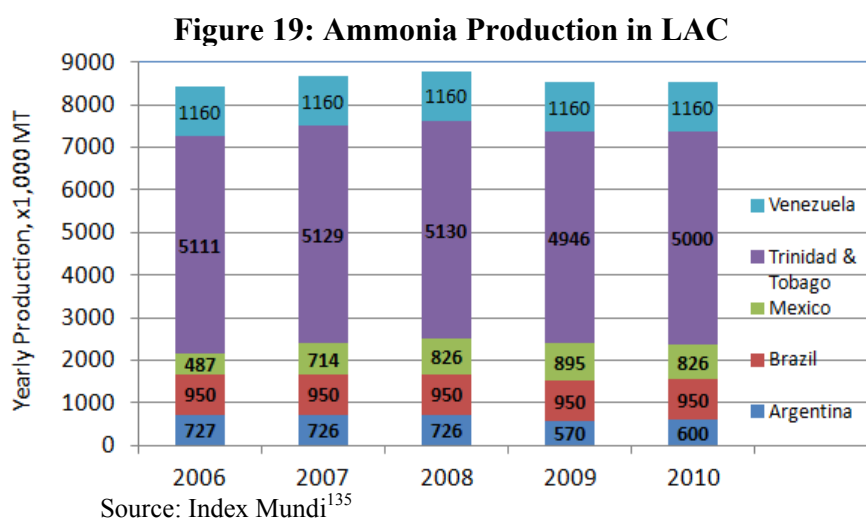
<sup>131</sup> Copplestone, J.C., Kirk, C.M., Death, S.L. et al.,  
“I-Chemicals-A-Ammonia and Urea,” <http://nzic.org.nz/ChemProcesses/production/1A.pdf>.

<sup>132</sup> Ibid.

<sup>133</sup> Ibid., 127.

### 3. Ammonia and Urea Fertilizer Production in LAC

From 2006 to 2010, worldwide global production of ammonia increased from 125 to 131 million MT. Figure 19 shows the LAC countries that have relatively significant production of ammonia (i.e., > 100,000 MT/yr), such as Trinidad & Tobago, Venezuela, Brazil, Mexico, and Argentina.<sup>134</sup> One may notice that T&T is, by far, the largest producer of ammonia in LAC.



With regard to urea and fertilizer production, Latin America showed relative growth during the 2002-2007 time frame. The total production increased at an annual growth rate of 3.5% during this period, reaching more than 6 million MT in 2007 (ca. 3.5% of world production). Nitrogen is the main fertilizer produced in Latin America, followed by phosphate and potash.<sup>136</sup> In terms of fertilizer production by the top five LAC countries for each product line, Table 21 was published in the literature.

<sup>134</sup> Ammonia: Estimated World Production, By Country, 2010. Index Mundi, [http://www.indexmundi.com/en/commodities/minerals/nitrogen/nitrogen\\_t12.html](http://www.indexmundi.com/en/commodities/minerals/nitrogen/nitrogen_t12.html).

<sup>135</sup> Ibid.

<sup>136</sup> Hernandez, M.A. and Torero, M. January 2011. "Fertilizer Market Situation - Market Structure, Consumption and Trade Patterns, and Pricing Behavior." International Food Policy Research Institute (IFPRI) Discussion Paper 01058, <http://www.ifpri.org/sites/default/files/publications/ifpridp01058.pdf>.



**Table 21: LAC Concentration of Fertilizer Production Capacity, 2008-2009**

Fertilizer	Top Five countries (% of region)	Top Five Capacity (000 MT)	Top Five Share (% of Region)	Top Five Share (% of World)
Ammonia	Trinidad and Tobago (48.3), Venezuela (17.5), Brazil (15.2), Argentina (8.1), Mexico (8.1)	10,739	97.0	6.5
Urea	Venezuela (36.8), Brazil (28.8), Argentina (19.6), Trinidad and Tobago (10.7), Mexico (3.2)	6,635	100.0	4.2
AN	Brazil (44.7), Chile (22.2), Cuba (13), Mexico (6.8), Colombia (5.1)	3,357	92.0	5.5
DAP/MAP	Brazil (70), Mexico (17.4), Venezuela (6.6), Peru (6)	1,669	100.0	4.8
Phosphoric acid	Brazil (79.3), Mexico (14.8), Venezuela (4.3), Bolivia (1.6)	1,923	100.0	4.2
Potash	Chile (64.7), Brazil (34.9), Colombia (0.4)	1,462	100.0	2.8
NPK	Brazil (55.4), Colombia (18.9), Venezuela (8.3), Ecuador (7.1), Chile (3)	3,676	92.0	3.9

AN = ammonium nitrate, DAP/MAP: di-ammonium and mono-ammonium phosphate,

NPK - nitrogen (N), phosphorus (P), and potassium (K)

Source: Hernandez and Torero<sup>137</sup>

The information in Table 21 shows that, for each type of fertilizer, more than 90% of LAC's production is concentrated in a maximum of five countries. Brazil is one of the top five producers of each fertilizer product.

#### 4. Ammonia and Urea Manufacturing Technologies

##### a. Ammonia Manufacturing Process

Most ammonia manufacturing technologies are derived from the original synthesis<sup>138</sup>—known as the Haber-Bosch process. It was named after the development work by Fritz Haber and Carl Bosch in 1909 and patented in 1910.

There are various technologies for manufacturing ammonia and its main derivative, urea, based on the chemical synthesis shown below. In the ammonia plant production process, the following process steps are carried out based on the Kellogg Brown & Root (KBR) Purifier™ ammonia process:<sup>139</sup>

<sup>137</sup> Ibid., 118.

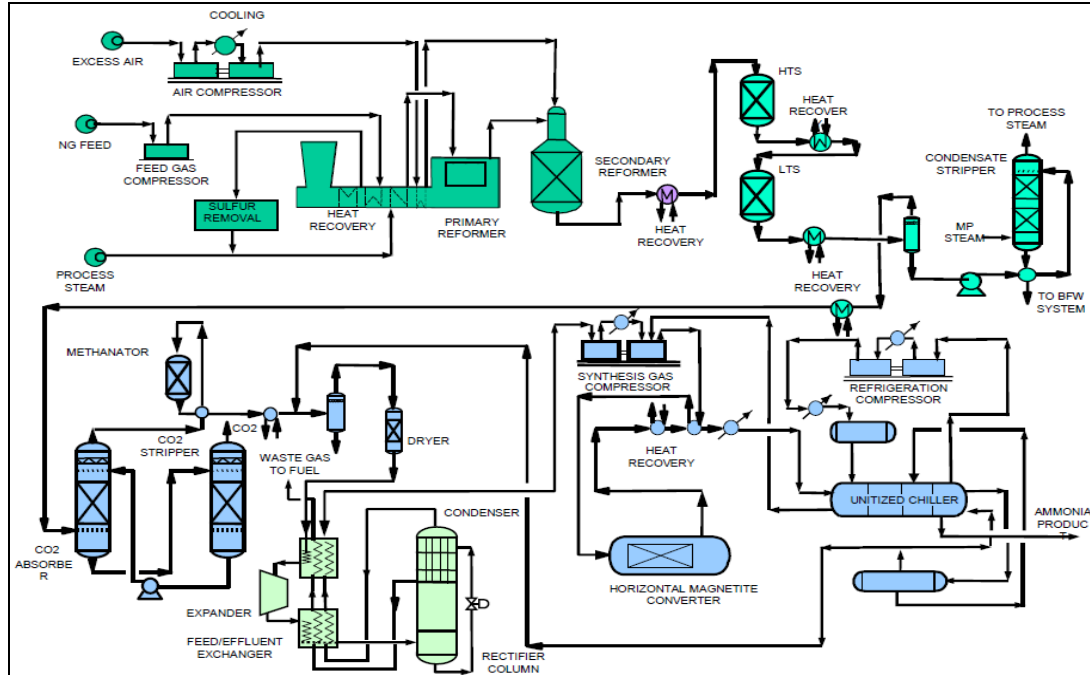
<sup>138</sup> Ammonia - <http://en.wikipedia.org/wiki/Ammonia>.

<sup>139</sup> Ammonium Nitrate Project 204 - Public Environmental Review, Ammonia, GHD, <http://apac.dynonobel.com/files/2010/12/Appendix-B-Process-Description.pdf>.

- a) A Desulfurizer, which consists of compressing and preheating natural gas, which is catalytically desulfurized.
- b) A Primary/Secondary Reformer, where the mixture of natural gas/steam is preheated and reacted with a nickel catalyst to convert methane into  $H_2$ ,  $CO_2$ ,  $CO$ , and some remaining  $CH_4$ . The process gas is then fed into the secondary reformer with excess air to complete this phase.
- c) Shift Conversion – After Step b above, the gas is fed into the waste heat recovery boiler and passes to the high temperature shift (HTS) and the low temperature shift (LTS) converters, respectively, whereby  $CO$  is converted into  $CO_2$ .
- d) Carbon Dioxide Removal, which is carried out by a two-stage process licensed by BASF.
- e) Methanation, where the concentration of both  $CO$  and  $CO_2$  is substantially reduced with a nickel-based catalyst;  $CO$  and  $CO_2$  are reacted with  $H_2$  to form  $CH_4$ .
- f) Drying and Purification, whereby the methanator effluent is cooled by methanator feed, cooling water, and ammonia refrigerant. The synthesis gas is then dried in molecular desiccant driers.
- g) Ammonia Synthesis, which is summarized in the second step of chemical synthesis. Basically, the synthesis gas is compressed and then heated before passing through an iron magnetite catalyst, where  $H_2$  and  $N_2$  are reacted to give ammonia.

The previous step-by-step ammonia production process is depicted in the flow chart in Figure 20.

### Figure 20: Purifier™ Ammonia Manufacturing Process

Source: GHD/KBR<sup>140</sup>

### b. Urea Manufacturing Processes

Urea is synthesized from ammonia and  $\text{CO}_2$ . This is the basis for all manufacturing technologies. In all  $\text{CO}_2$  stripping methods, ammonia and  $\text{CO}_2$  are fed into the synthesis reactor, and ammonium carbamate is produced. The second step consists of dehydration of carbamate to urea and  $\text{H}_2\text{O}$ . This is a summary of the manufacturing process for urea.<sup>141</sup>

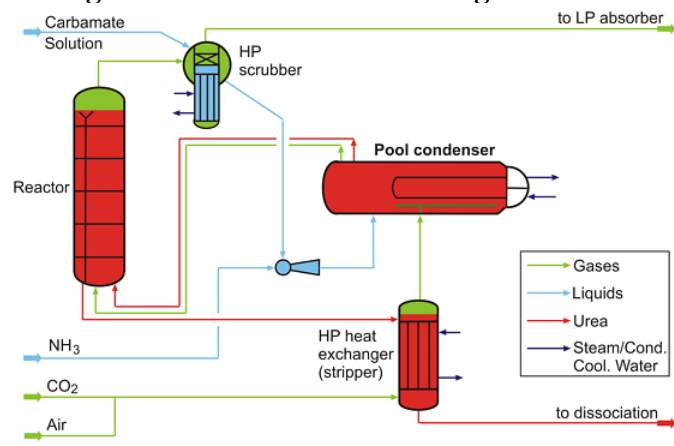
A typical plant process for urea manufacturing, licensed by Uhde, is shown in the flow chart in Figure 21.<sup>142</sup>

<sup>140</sup> Ibid.

<sup>141</sup> “Urea synthesis with pool condenser.” (Stamcarbon Urea 2000plus™ technology) 2012. ThyssenKrupp Uhde GmbH, <http://www.uhde.eu/competence/technologies/fertiliser/ammonia-urea/169/171/urea-synthesis-with-pool-condenser.html>.

<sup>142</sup> Ibid.

**Figure 21: Urea Manufacturing Process**



Source: Uhde<sup>143</sup>

## 5. Energy Intensity and CO<sub>2</sub> Emissions from Ammonia and Urea Manufacturing Plants

In a 2008 benchmark study<sup>144</sup> of energy intensity and CO<sub>2</sub> emissions from ammonia plants, the Canadian Office of Energy Efficiency reported that the natural gas-based plants use an average of 34.4 GJ/t NH<sub>3</sub>. The lowest energy intensity for all plants was 29.7 GJ/t NH<sub>3</sub>. The CO<sub>2</sub> generated by the plants was in the range of 1.66 to 1.98 t CO<sub>2</sub>/t NH<sub>3</sub>. The same study also reported that about 40% of the CO<sub>2</sub> generated by the ammonia plants was recovered in the urea manufacturing process.

Another 2008 study reported by the International Fertilizer Industry Association (IFA)<sup>145</sup> suggested that the average energy intensity of 93 ammonia plants was 36.6 GJ/t NH<sub>3</sub> (ranging from 27.0 to 58.2 GJ/t NH<sub>3</sub>), while the top quartile performed in the range of 28 to 33 GJ/t NH<sub>3</sub>.

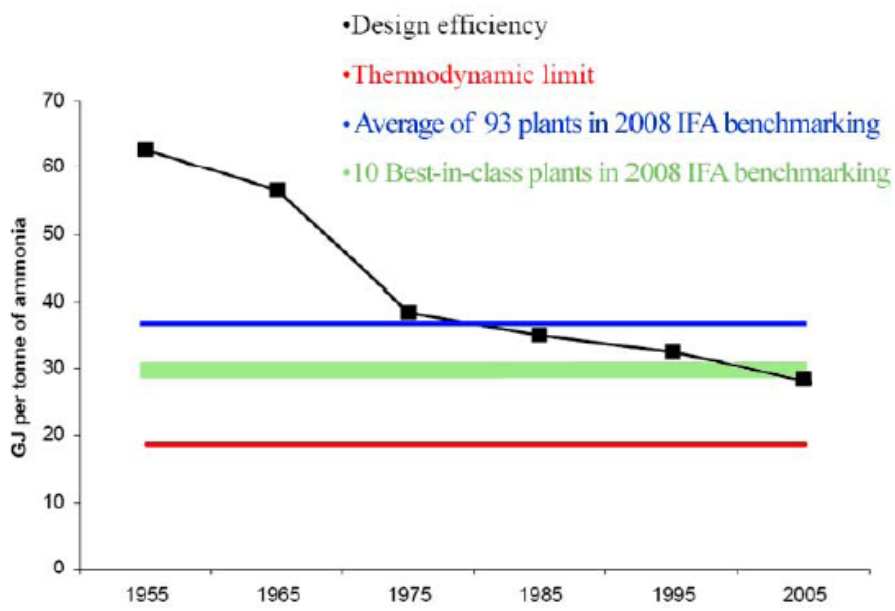
<sup>143</sup> Ibid.

<sup>144</sup> "Benchmarking Energy Efficiency and Carbon Dioxide Emission, Canadian Ammonia Producers." 2008. Prepared for the Canadian Fertilizer Institute and Natural Resources, Canadian Industry Program for Energy Conservation, Office of Energy Efficiency, c/o Natural Resources Canada, <http://oee.nrcan.gc.ca/sites/oee.nrcan.gc.ca/files/pdf/industrial/technical-info/benchmarking/ammonia/pdf/ammonia-study.pdf>.

<sup>145</sup> "Energy Efficiency and CO<sub>2</sub> Emissions in Ammonia Production." *Summary Report, 2008-2009*. International Fertilizer Industry Association (IFA), [http://www.fertilizer.org/ifacontent/download/26110/374422/version/1/file/2009\\_tech\\_energy\\_efficiency.pdf](http://www.fertilizer.org/ifacontent/download/26110/374422/version/1/file/2009_tech_energy_efficiency.pdf).

The highlights of the IFA study are shown in Figure 22.

**Figure 22: Improved Energy Efficiency of Ammonia Plants (1955-2005)**



Source: IFA<sup>146</sup>

The chart in Figure 22 suggests an average specific energy consumption of 30 GJ/t NH<sub>3</sub> for “Best-in-Class” plants, while the thermodynamic limit was ca. 18 GJ/t NH<sub>3</sub>. This is in line with the aforementioned data reported for the Canadian plant survey.<sup>147</sup>

In a 2005 IEA study<sup>148</sup> of the energy intensity of ammonia plants, the energy intensity of natural gas-based plants was as follows:

Western Europe:	35 GJ/t NH <sub>3</sub>
North America:	37.9 GJ/t NH <sub>3</sub>
Latin America:	36 GJ/t NH <sub>3</sub>

<sup>146</sup> Ibid.

<sup>147</sup> Ibid., 148.

<sup>148</sup> International Energy Agency. 2007. *Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions*. ENERGY, INDICATORS, © OECD/IEA, [http://www.iea.org/textbase/nppdf/free/2007/tracking\\_emissions.pdf](http://www.iea.org/textbase/nppdf/free/2007/tracking_emissions.pdf).

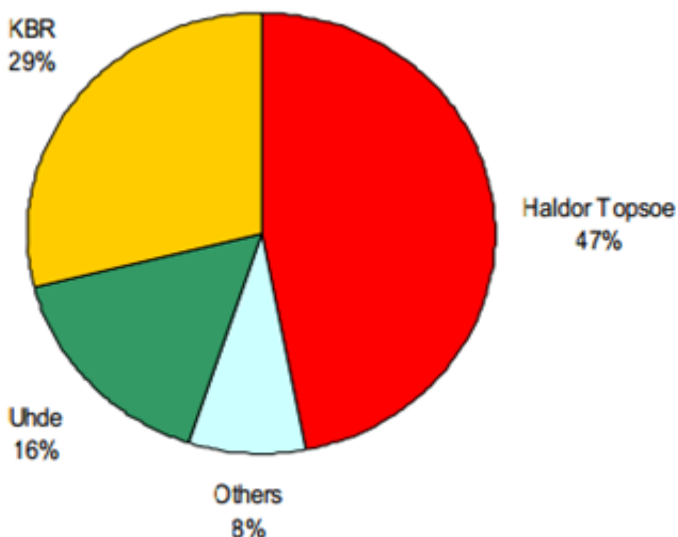
The data above suggest that the energy intensity of Latin American plants is comparable to that of Western Europe and North America, with the figures from all three regions being within a few percentage points of one another.

## 6. Commercial Technology Licensors

There are a few well-known technology licensors of ammonia manufacturing technologies, such as KBR, Haldor Topsoe A/S, the Linde Group, Lurgi AG, and Uhde. These are basically the same licensors as those presented earlier for methanol production technology. Although most ammonia technologies are based on the original Haber-Bosch process, they do have some differentiation in operating conditions and catalyst technology, which are generally kept proprietary. The same can be said for urea production as a derivative of ammonia manufacturing.

In terms of the competitive landscape between the various ammonia/urea production technologies, some published information suggests that the 2007 market shares were those presented in Figure 23.<sup>149</sup>

**Figure 23: Ammonia Licensors' Market Shares (2007)  
(Plants Built Since 1990)**



Source: Nexant<sup>150</sup>

<sup>149</sup> "PERP Program – Ammonia." 2007. ChemSystems, Nexan Inc., [http://www.chemsystems.com/reports/search/docs/abstracts/0506S11\\_abs.pdf](http://www.chemsystems.com/reports/search/docs/abstracts/0506S11_abs.pdf).

The chart in Figure 23 suggests that Haldor Topsoe A/S had a leading position, followed by KBR and Uhde.

### **III. Benchmarks and Guidelines for Future Petrochemical Plants**

#### **1. Benchmark Factors and Guidelines for Steam Crackers**

In Section II.A we highlighted all of the important parameters that characterize an acceptable steam cracker, based on the state-of-the-art design technologies. This includes the technical characterization of an appropriate cracker in terms of energy intensity, CO<sub>2</sub> emissions, HVC yield, and typical investment costs for a given plant capacity.

The specific contributions of the various cracker components and hardware in terms of energy consumption, CO<sub>2</sub> emissions, and investment costs were also discussed. These considerations would be utilized as supportive references for a prospective steam cracker evaluation and analysis.

The performance of the prospective LAC steam cracker can be expressed in terms of the SEC (energy consumed by the cracker per kg of HVCs produced), CO<sub>2</sub> emissions (t CO<sub>2</sub>/t HVC), and the HVC yield. Instead of evaluating each factor as a potential benchmark separately (one at a time), it may be more useful to define a factor that groups the three parameters, as they are somewhat related.

Accordingly, the following benchmark factor (BF) can be utilized:<sup>151</sup>

$$BF = HVC / (CF \times SEC)$$

Where:

BF= Benchmark factor

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<sup>150</sup> Ibid.

<sup>151</sup> Caroline, D. and Turner, G. March 2006. Documentation: Petrochemicals EU ETS Phase II New Entrants Supporting, <http://webarchive.nationalarchives.gov.uk/+/http://www.berr.gov.uk/files/file28616.pdf>.

HVC = Yield (% of mass of HVCs per plant production)

CF= CO<sub>2</sub> emissions (t CO<sub>2</sub>/t HVC)

SEC= Specific energy efficiency (GJ/t HVC)

In computing the BF<sub>s</sub> for the ethane-fed cracker and the naphtha-based cracker from the information in Table 15, we obtain the information in Table 22.

**Table 22: Benchmark Data for Steam Crackers**

	Ethane	Naphtha
HVC (% wt)	0.82 min.	0.55 min.
CF, CO <sub>2</sub> Emissions (t CO <sub>2</sub> /t HVC)	1.1 max.	1.7 max.
SEC (GJ/t HVC)	17.5 max. .	15.5 max.
BF	0.043 max.	0.021 max.

These BF<sub>s</sub> can be utilized in future plant designs to ensure that the designs meet the criteria of the appropriate plant in terms of HVC yields, CO<sub>2</sub> emissions, and SECs for a given plant capacity.

These calculations in table 22 are for guidance only. The detailed design of the furnaces and downstream components, along with operating conditions, may have other effects on the final plant characteristics.

## 2. Energy Intensity Benchmarking for PE/PP, Methanol, and Ammonia/Urea Plants

### a) Polyethylene and Polypropylene Plants

In Subsection II B.the 2006 Weighted EU Average for European plants suggested the energy intensity data in Table 23.

**Table 23: Energy Intensity for PE and PP Weighted EU Averages**

LDPE High Pressure Process (Tube and Batch Reactors)	8.53 (GJ/MT)
HDPE Low Pressure Process (Suspension and Gas-Phase Processes)	5.43 (GJ/MT)
Polypropylene (Suspension and Gas-Phase Processes)	3.56 (GJ/MT)

Source: Schyns<sup>152</sup>

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<sup>152</sup> Schyns. December 2006. "Feedstock Substitutes, Energy Efficiency Technologies and CO<sub>2</sub> Reductions in Petrochemical Products." Presentation at the IEA/CEFIC Workshop Feedstock Substitutes. Paris, France.



The energy intensity data in Table 23 were deemed to be about 30% higher than the EU Best Practice technology. As benchmarks for LAC plants, one can utilize the Weighted EU Averages above, as they represent the appropriate use of available technologies.

b) Methanol Plants

In Subsection II.C, some energy intensity data for methanol plants were reported. More specifically, the 2007 data reported by the IEA and Lurgi GmbH (2006) suggested the summary information in Table 24.

**Table 24: Summary of Energy Intensity for Methanol Plants**

Typical Methanol Plant:	30 GJ/MT
“Best-in-Class” (BIC) Plant:	28.5 GJ/MT
Theoretical Minimum Energy Intensity:	20 GJ/MT

Source: <sup>153</sup>IEA, <sup>154</sup>Lurgi

The above “Best-in-Class” (BIC) energy intensity of 28.5 GJ/MT can be utilized for future LAC plant benchmarking purposes. The main reason that we are proposing the BIC benchmark is that it represents the achievable energy intensity, according to Lurgi GmbH, a prominent technology licensor of large-scale, autothermal reforming plants.

c) Ammonia/Urea Plants

In compiling the energy intensity data reported in Subsection II.D, we noted the information on the energy intensity of ammonia plants found in Table 25.

**Table 25: Energy Intensity of Ammonia Plants**

Canadian Office of Energy Efficiency Survey (2008):	29.7 GJ/t NH <sub>3</sub> “Best-in-Class”
International Fertilizer Industry Association (2008):	28 GJ/t NH <sub>3</sub> “Best-in-Class”
IEA (2005):	35 to 38 GJ/t NH <sub>3</sub> Range for Worldwide Natural Gas Plants
IEA (2005):	36 GJ/t NH <sub>3</sub> for Latin America

Source: <sup>155</sup>COEE, <sup>156</sup>IFA, <sup>157</sup>IEA

<sup>153</sup> Ibid., 152.

<sup>154</sup> Ibid., 119.

The data in Table 25 suggests that a 30 GJ/t NH<sub>3</sub> plant energy intensity can be utilized as a benchmark for future LAC plants. This represents the achievable energy intensity as shown by Canadian plant surveys.

#### **IV. Conclusion**

##### **Ethylene Steam Crackers and Petrochemical Plants**

- The foregoing analysis showed that CO<sub>2</sub> is the overwhelming GHG emission gas for petrochemical plants—namely, CO<sub>2</sub> makes up 99% of GHGs.
- The steam cracking furnace is the most energy intensive of all of the plant components; it emits the most CO<sub>2</sub> emissions.
- The steam cracker technology vendors and licensors have comparable designs; differentiation features may not have a significant impact on specific energy consumption and CO<sub>2</sub> emissions.
- Plant scale has a positive effect on initial plant investment and plant operating costs—“The Bigger the Better.”
- New plant design and engineering in LAC can benefit from the state-of-the-art technologies for steam cracker components—especially the “pyrolysis furnace” section, the most energy intensive emitter of CO<sub>2</sub>.
- LAC plant designs can take advantage of the benchmark factors for plant HVC yield, CO<sub>2</sub> emissions, and SECs. These can be utilized as guidelines for future plant design and construction.

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<sup>155</sup> Ibid., 118.

<sup>156</sup> Ibid., 149.

<sup>157</sup> Ibid., 152.

- Brazil and Mexico and, to a lesser extent, Chile and Argentina have a fully integrated petrochemical process (“cradle to grave”)—namely, significant crude oil/gas E&P sources, refining capacities, steam cracking capabilities, processing of various HVCs, and a sizable consumer product market (to absorb new production). This suggests that these countries may be good candidates for the location of the prospective plant.

### **PE/PP Plants**

- There are two main manufacturing processes: high pressure and low pressure. The low pressure process (gas-phase technology), which can utilize a wide range of catalysts, is the most widely utilized manufacturing process in state-of-the-art ethylene to PE conversion plants.
- In terms of global production growth, PP, HDPE, and LLDPE have experienced the fastest increase over the last 10 years.
- The energy intensity for manufacturing LDPE is almost twice as high as it is for HDPE. The energy intensity for the production of HDPE is higher than it is for polypropylene.
- As energy intensity benchmarks for LAC plants, one can utilize the reported Weighted EU Averages, as they represent the appropriate use of available technologies.

### **Methanol Plants**

- Methanol can be produced from a very wide range of feedstocks, namely, natural gas, coal, biomass, agricultural and timber waste, and solid municipal waste. However, overall, natural gas conversion to methanol is the most efficient.
- The typical manufacturing process of methanol generally requires two steps, namely, conversion of natural gas into a stream composed of CO, CO<sub>2</sub>, H<sub>2</sub>O, and hydrogen, which is followed by catalytically synthesizing methanol from the synthesis gas.

- Literature data suggest an achievable energy intensity of 28.5 GJ/MT; this level can be utilized for benchmarking purposes in future LAC plants.

### **Ammonia/Urea Plants**

- Ammonia is one of the largest chemicals manufactured from hydrocarbons. It is the main element in the value chain for producing fertilizers such as urea fertilizer and a wide range of industrial applications.
- Ammonia is synthesized from the hydrogen contained in natural gas (main feedstock) and the nitrogen contained in air; urea is synthesized from ammonia and carbon dioxide.
- For each fertilizer product, more than 90% of LAC production is concentrated in a maximum of five countries. Brazil is one of the top five producers of each fertilizer product.
- Based on data published by COOE, the IFA, and the IEA, a 30 GJ/t NH<sub>3</sub> plant energy intensity can be utilized as a benchmark for future LAC plants.