Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals

Edited by Richard G. Herman

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DEDICATION BY THE EDITOR

Dedicated to my scientific mentors, Abraham Clearfield, Sten Ahrland, Jack H. Lunsford, and Kamil Klier, who, with patience, perseverance, and example, provide continual encouragement, to my inspirational academic great-grandfather, Linus Pauling, to an inspirational great-grandfather of catalysis, Paul H. Emmett, and to the past and present faculty, especially of the Chemistry Department, at Fredonia State University College, who teach the heart and mind that, with study, effort, and optimism, nearly all goals are attainable.

PREFACE

Most of the papers contained in this volume are based on presentations made at the symposium on Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals, which was held at the 17th Middle Atlantic Regional Meeting of the American Chemical Society, April 6-8, 1983, in the setting of the Pocono Hershey Resort, White Haven, PA. I thank Dr. Ned D. Heindel, General Chairman, and Dr. Natalie Foster, Program Chairman, both of Lehigh University, for the invitation to organize the symposium. Financial support was received from Air Products and Chemicals, Inc. for the organization of the symposium, and acknowledgement is made to Air Products and Chemicals, Inc. and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the conduct of the symposium.

The theme of this volume is the recent progress made in developing and understanding viable catalytic syntheses of chemicals directly from synthesis gas ($CO + H_2$) or indirectly via alcohols. An aim of the symposium and of this volume is to provide a meaningful blend of applied and basic science and of the chemistry and engineering of processes that are, or hold promise to be, economically and industrially feasible. The topics demonstrate the increasing importance of synthesis gas as a versatile feedstock and emphasize the central role that alcohols, such as methanol, can play as chemical intermediates. Although recent developments in, and new perspectives of, established processes are presented, the emphasis is to provide insights into processes that are still in the research, development, and scale-up stages.

The practical orientation of this volume is directed towards professional chemists and engineers. However, the papers are written in an instructional fashion so that this volume can be used as a complementary reference book in advanced undergraduate or graduate courses in catalysis.

I wish to thank Dr. Henry Leidheiser, Jr., Director of the Center for Surface and Coatings Research at Lehigh University from 1968 to 1983, for his continuous encouragement and support. Appreciation is

extended to all of the authors for their pleasant and timely cooperation and for their efforts in producing quality papers. I especially appreciate and thank my wife, Helen Lynn, for her assistance in the formatting of this volume and for typing the final copy.

Richard G. Herman
September 1, 1983

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INTRODUCTORY ORIENTATION

PERSPECTIVES ON THE UNITED STATES FEEDSTOCKS FOR THE PRODUCTION OF ENERGY AND CHEMICALS

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INTRODUCTION

We tend to think of energy as power that is consumed to provide us with services, e.g. electricity for lighting, fuel oil for heat, and gasoline for transportation, and of chemical feedstocks as raw materials that are transformed into industrial or consumer goods. However, energy and chemical feedstocks are not exclusive categories because both are based principally on the same natural resources. Coal, crude oil, and natural gas provide raw materials for industry, as well as the energy to process the materials into commodities. It will become clear in the following discussion that energy, industry, consumer goods, and the standard of living are intimately entwined.

SOURCES OF ENERGY

To carry out its daily functions, the human body consumes about 3000 kcal, or approximately 12,300 Btu, of energy. Of course, we enjoy eating and drinking to provide this energy, wherein our bodies transform the food into energy. This quantity of energy is equivalent to the energy contained in one lb of bituminous coal. However, to maintain our standard of living in the United States today, the per capita energy consumption is equivalent to about 12 short tons of coal annually [1]. This 300 million or so Btu quantity of energy is used for transportation, to run our households, to operate our business establishments, and by our industrial sector. It has been noted that this per capita energy usage is equivalent to each of us having 1200 personal slaves [2].

From where is this energy derived? It is obtained mainly from the storehouse of fossil fuels - coal, crude oil, and natural gas. Figure 1 shows the apportionment of natural resources that are used to generate energy in the United States. A similar figure could be constructed to represent the world energy patterns [3], although the early usage of coal would be at a larger percent of the total, while the contribution of petroleum would occur somewhat later and would be of a slightly smaller magnitude. It is clear from Figure 1 that the source of U.S. energy shifted from wood to coal in the late 1800's, most noticeably in the 1880-1895 period, and shifted again after World War II from coal to petroleum and natural gas. The contribution of nuclear power has been steadily increasing, while hydro-derived power has maintained a constant portion of the energy supply.

Nuclear and Hydroelectric Power

Subsequent discussion will center on coal, petroleum, and natural gas since these resources can be used to produce chemicals, as well as energy. Nuclear power and hydroelectric power are devoted to the generation of electricity, and the role of these in electrity generation will be briefly discussed to provide a perspective on the part that these play in the balancing of energy resources. The annual production of consumable electric energy in the U.S. has stabilized at about 2,300 billion kilowatt hour (kWh), which is equivalent to 11.2 x 10^{15} Btu or 11.2 Quads. To generate this electricity, large quantities of fuels are consumed in a rather inefficient manner because of conversion and transmission losses. In fact, it requires about 10,000 Btu's to deliver one kWh of electricity [4]. This corresponds to a 60-67% loss of the energy contained in the original fuel. Therefore, it now takes about 3.3 Quads of nuclear energy and 3.3 Quads of hydroelectric power, as well as on the order of 13 Quads derived from coal, 4 Quads produced from petroleum, and 4.5 Quads obtained from natural gas to generate the quantity of electricity annually utilized in the U.S. Thus, appreciable consumption of fossil fuels is necessary to satisfy the demand for electricity.

This distribution of fuels to generate electricity is the average for the U.S. Some states, e.g. Illinois, depend heavily on nuclear power generated electricity, while others, such as those associated with the Tennessee Valley Authority, rely on hydroelectric power. Still others, such as the states bordering on the Ohio Valley derive electricity from coal-fired power plants. This leads to differences in the cost of electricity to the consumers in the various areas of the U.S. An estimate of comparative costs is given in Table 1, and it is indicated that electricity can be produced from coal-fired and nuclear power plants for about the same cost of 38-39 mills/Kwh. This assumes that coal can be obtained at $40/ton and that the nuclear plant construction lead time is maintained at only six years. If the price of coal rises to $65/ton, the fuel cost increases to 26.0 mills/Kwh, which results in a total cost for the

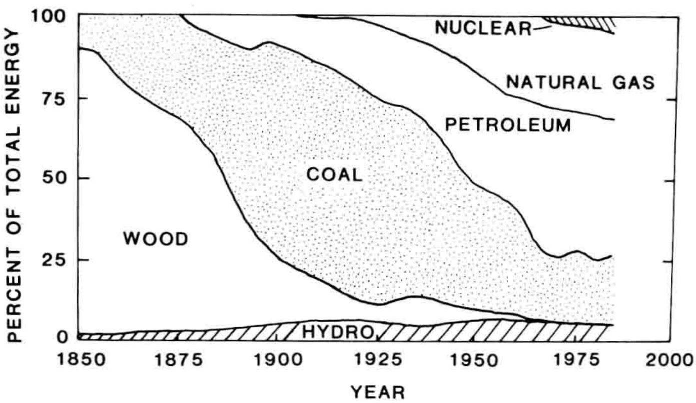

Figure 1. The historical pattern of energy utilization in the United States.

generated electricity of 48.2 mills/Kwh [5]. If the construction lead time for the nuclear power plant is drawn out to 10 years, the total cost of the produced electricity will increase by approximately 25% to about 49 mills/Kwh.

During the last decade, the price of coal has been increasing in conjunction with the increased cost of crude oil, although not as rapidly. This has led to even more favorable comparative economics for utilizing nuclear power to generate electricity in Western Europe and Japan. This point was initially emphasized by the very large price increase for crude oil that was enforced by the OPEC[a] nations in 1973. During the following year, there were 62 nuclear power reactors ordered or letters of intent placed by the OECD[b] countries. Of course, with a six year lead time, these plants would not begin to come on stream until 1980. Between 1974 and 1980, however, new governmental regulations, increased lead time and costs, and, due in part to conservation, the average annual increase in electricity demand by OECD nations dropped from the high demand rate of about 7% annually in the 1960-1973 period to 3.1% [6]. This led to the deferment or cancellation of 71 nuclear power projects in the U.S. during 1974-1981 [6]. This compares with the 72 operating nuclear power reactors at the end of 1978 [7]. The trend in the U.S. for new elec-

[a]Organization of Petroleum Exporting Countries (OPEC): Algeria, Ecuador, Gabon, Indonesia, Iraq, Iran, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, the United Arab Emirates, and Venezuela.

[b]Organization for Economic Cooperation and Development (OECD): Australia, Austria, Belgium, Canada, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Japan, Luxembourg, Netherlands, New Zealand, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, United Kingdom, and the United States.

Table 1. Comparative Cost Estimates (1981:mills/Kwh) for Electricity Generated from High Sulfur Fuel Oil, Nuclear Power, and Coal [adapted from Reference 5].

	Oil[a]	Coal[a]	Nuclear[b]
Plant size (megawatt)	600	600	1100
Capital cost	12.9	17.1	24.8
Operating cost[c]	4.2	5.1	4.2
Fuel cost	47.6	16.0	10.0
TOTAL COST	64.7	38.2	39.0
Capital investment ($/Kw)	692	920	1331
Construction lead time (yr)	3	4	6
Fuel cost	$27/bbl	$40/ton	-
Relative cost[d]	194	60	40
Conversion efficiency(%)	35	60	40

[a]With flue gas desulfurization
[b]Pressurized water reactor
[c]Capacity factor of 65% for 30 years
[d]$ per ton oil equivalent

trical capacity is now away from nuclear power and toward coal-fired generation plants. For example, from mid 1983 to 1988, 50 nuclear plants are scheduled to start up, as well as 52 new coal-fired installations [8]. Past that date, 11 nuclear power plants are still on the drawing boards, while 72 coal-based plants are in the planning stage [8].

This situation is of special concern when considering fuels utilization, developments in the mining of coal, distribution of electrical power, and possible safety and environmental problems connected with the coal indistry. Of more immediate concern is the fiscal stability of the capital intensive nuclear power industry. As of December 31, 1981, the 76 U.S. nuclear power reactors (not plants) were located in 27 states and had a 74,000,000 kW operable capacity [9]. Most of these were associated with public utility systems that were or had been constructing or had planned additional nuclear reactors. Many of these additions were abandoned but were still a financial liability because of the debt incurred in these projects. This culminated in August 1983 when the Chemical Bank of New York filed suit against the Washington Public Power Supply System (WPPSS) seeking to recover a $2.25 billion debt from the largest bond default in U.S. history [10]. The WPPSS had developed a $24 billion construction program to build five nuclear power plants, and one of those will begin operation in 1984. It should be noted that 13 of the 36 largest hydroelectric plants, with a combined installed capacity of 39,790,000 kW for the 36 plants, in the U.S. are located in the state of Washington [9].

Fossil Fuels and Economics

From this discussion, it can be concluded that nuclear energy will not appreciably increase its percentage of the total energy consumed in the U.S. in the near future (Figure 1), and it will not alleviate the demand for fossil fuels. Figure 2 depicts the trend of energy consumption in the U.S. for the last 33 years. It is evident that since the Middle East disruption of 1973, the consumption of energy has stabilized in the 70-80 Quad range, where 1 Quad = 1 quadrillion Btu. The energy produced in this country, however, does not fulfill the demand, and Figure 2 shows that since 1957, the U.S. has been an energy importing nation. Figure 2 also shows that petroleum is the dominant fuel in satisfying the U.S. energy demand. Although the U.S. continued to export coal, mainly to Europe and Japan, the importation of petroleum steadily increased until 1977 when about 45% of the domestic oil demand was met by imported crude oil. This resulted in a significant drain on the U.S. economy because fully 25% of the 76.3 Quads of energy consumed was derived from imported petroleum, which resulted in a massive cash flow from the U.S.

At the same time that U.S. crude oil imports were increasing, the price was also increasing. This is shown in Figure 3, where a barrel of petroleum contains 42 U.S. gallons. The most immediate and personal impact of the price increase of crude oil was the accompanying increase in the price of gasoline. It can be noted from Figure 3 that the % increase in the price of a gallon of gasoline was not even near to the % increase in the cost of a barrel of gasoline. Part of this is due to the taxation contained in the price of gasoline, e.g. in 1973, 38% of the real price of a gallon was added as tax [11]. Thus, the "real" cost of gasoline in 1973 was approximately $.27/gallon. In 1980, the % tax in gasoline prices was only 13% in the U.S., that is a real price of $1.06 plus $.14 tax for a selling price of $1.20/gallon. In 1973, gasoline prices in Europe, and most other countries of the world, were already over $1/gallon because of taxation. For example, in Germany 239% of the "real" cost of gasoline was added to the price as tax. Even so, the price of gasoline only increased about 3.5-fold in the 1973-1980 period, while the cost of imported crude oil increased over 10-fold.

On the other hand, industrial oil prices increased at double the rate of the gasoline price increase. One reason for this was that drivers could easily refuse to consume as many gallons of gasoline as they might otherwise have done, and this was particularly true in the U.S. as compared to most other OECD countries. However,

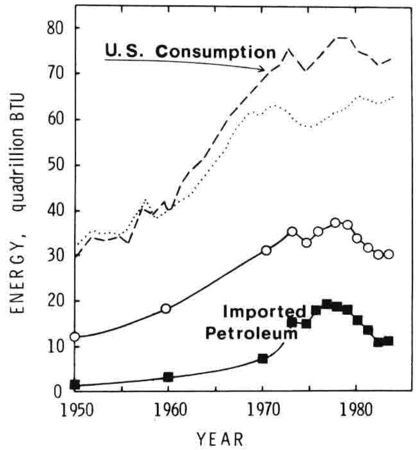

Figure 2. Comparison of the production (...) and consumption (---) of energy in the United States shows that the U.S. is a net importer of energy. The energy produced from imported petroleum (■) can be compared with the total quantity of energy derived from petroleum (O).

utilities and industries could not decrease their consumption of petroleum products without decreasing their goods and services. They basically comprised a captive market because they could not readily apply interfuel substitution. The same was true of the U.S. residential sector of the economy.

A barrel of crude oil is refined into a variety of products, and, contrary to what might be believed, an incoming tanker of crude oil cannot be converted into an outgoing tanker of gasoline. Typically, only 15% of a barrel of crude oil is refined into gasoline. Other fractions include 37.4% middle distillates consisting of domestic heating fuel oil, diesel fuel, jet fuel, and lubricants, 31% industrial boiler fuel (high sulfur fuel oil), 3.2% liquified petroleum gas (LPG), 0.8% asphalt and tar products, 6.5% naphtha, and 6.1% refinery fuel and losses. Most of these fractions suffered price increases that were greater than those for gasoline.

Naphtha is a primary chemical feedstock, and it can be easily thermally or catalytically cracked to olefins and other petrochemicals. Of the olefins, ethylene can be converted to polyethylene, ethylene oxide and ethylene glycol, and vinyl chloride and styrene monomers, while propylene can be transformed into polypropylene, acrylonitrile, isopropanol, propylene oxide, and many other basic chemicals. Naphtha can also be reformed into the xylenes, toluene, and benzene. It can also be catalytically reformed into synthesis gas. Thus, naphtha is a cornerstone of the U.S. chemical industry.