

# Tri-reforming: A New Process Concept for Effective Conversion and Utilization of CO<sub>2</sub> in Flue Gas from Electric Power Plants

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## INTRODUCTION

CO<sub>2</sub> conversion and utilization are a critically important element in chemical research on sustainable development. The prevailing thinking for CO<sub>2</sub> conversion and utilization begins with the use of pure CO<sub>2</sub>, which can be obtained by separation. In general, CO<sub>2</sub> can be separated, recovered and purified from concentrated CO<sub>2</sub> sources by two or more steps based on either absorption or adsorption or membrane separation. These separation and purification steps can produce pure CO<sub>2</sub> from flue gases of power plants but add considerable cost to the CO<sub>2</sub> conversion or sequestration system [DOE/OS-FE, 1999]. Even the recovery of CO<sub>2</sub> from concentrated sources requires substantial energy input [Weimer et al., 1996]. According to US DOE, current CO<sub>2</sub> separation processes alone require significant amount of energy which reduces a power plant's net electricity output by as much as 20% [DOE/FE, 1999a]. While new technology developments could make this recovery easier to handle and more economical to operate in power plants, it is highly desirable to develop novel ways to use CO<sub>2</sub> in flue gases without separation.

## SOURCES OF CO<sub>2</sub> EMISSIONS

A recent paper showed the data on CO<sub>2</sub> emissions from the consumption of fossil fuels during 1980-1997 in the world based on government reports on statistics [EIA/IEO, 1998, 1999]. The three major fossil fuels used worldwide are coal, petroleum, and natural gas. A very large amount of CO<sub>2</sub> is emitted every year, and the total amount of annual emissions is also increasing rapidly. The current top 10 major producers of CO<sub>2</sub> in terms of total annual emission include US, China, Russia, Japan, India, Germany, UK, Canada, South Korea, and Italy. CO<sub>2</sub> emissions from many other countries, particularly developing countries, are increasing rapidly.

Table 1 CO<sub>2</sub> Emissions from Different Sectors in the U.S. (in Million Metric Tons of Carbon)

CO <sub>2</sub> Emissions Sources	1980	1985	1990	1995	1997
CO <sub>2</sub> from Residential Sector	248.4	245.8	253.1	270.3	286.5
CO <sub>2</sub> from Commercial Sector	178.3	189.7	206.8	217.9	237.2
CO <sub>2</sub> from Industrial Sector	484.6	424.7	454.1	465	482.9
CO <sub>2</sub> from Transportation Sector	378.1	384.4	432.1	458.5	473.1
CO <sub>2</sub> from End-Use Total	1289.4	1244.6	1346.1	1411.7	1479.6
CO <sub>2</sub> from Electric Utilities*	418.4	439	476.9	495.3	523.4

\*Electric Utility emissions are distributed across end-use sectors.

Sources: DOE, EIA, 1998, 1999

Table 1 summarizes the CO<sub>2</sub> emissions from different sectors in the U.S. [EIA/AER, 1998, 1999]. A clear trend is that all the end-use sectors of energy are major contributors of CO<sub>2</sub>, and electric power industry is no longer the only major CO<sub>2</sub> emitter. In other words, everyone in the society is responsible for the increased CO<sub>2</sub> production, either by using electricity in various places and by consuming fuels for transportation and for other purposes. Table 2 specifically indicates the CO<sub>2</sub> emissions from the U.S. electricity-generating units in electric utilities and non-utilities based on coal, natural gas and petroleum [EIA/AER, 1998, 1999]. Coal is the dominant fossil fuel for the electricity-generating units. On the other hand, it is projected that the share of natural gas-fired units will increase significantly in the near future, due to the heightened concerns for environmental issues and the fact that natural gas is viewed as a premium fuel and is environmentally cleaner than either coal or petroleum.

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**Table 2. CO<sub>2</sub> Emission from Electricity-Generating Units in the U.S. (in Million Metric Tons of Carbon)**

CO <sub>2</sub> Emissions Sources	1990	1995	1997
Coal-Fired Units at Electric Utilities	409.9	434.3	471.3
Petroleum-Fired Units at Electric Utilities	25.3	13.0	15.0
Gas-Fired Units at Electric Utilities	39.2	44.5	36.0
Other Units at Electric Utilities	1.2	0.8	1.0
<b>Emissions at Electric Utilities, Total</b>	<b>475.5</b>	<b>492.7</b>	<b>523.4</b>
Coal-Fired Units at Nonutilities	17.8	24.6	25.3
Petroleum-Fired Units at Nonutilities	4.3	7.3	7.4
Gas-Fired Units at Nonutilities	39.2	57.6	53.2
Other Units at Nonutilities	37.4	45.9	48.4
<b>Emissions at Nonutilities, Total</b>	<b>98.7</b>	<b>135.5</b>	<b>134.4</b>
CO <sub>2</sub> from Coal-Fired Units, Total	427.7	458.9	496.6
CO <sub>2</sub> from Petroleum-Fired Units, Total	29.6	20.3	22.4
CO <sub>2</sub> from Gas-Fired Units, Total	78.4	102.1	89.3
CO <sub>2</sub> from Other Units, Total	38.5	46.8	49.4
<b>Total CO<sub>2</sub> Emissions from Generators</b>	<b>574.2</b>	<b>628.1</b>	<b>657.7</b>

Sources: DOE, EIA, 1998, 1999

### ADVANTAGES OF USING FLUE GAS FOR CO<sub>2</sub> CONVERSION

As can be seen from Table 2, flue gases from fossil fuel-based electricity-generating units represent the major concentrated CO<sub>2</sub> sources in the US. If CO<sub>2</sub> is to be separated, as much as 100 megawatts of a typical 500-megawatt coal-fired power plant would be necessary for today's CO<sub>2</sub> capture processes based on the alkanolamines [DOE/FE, 1999a]. Therefore, it would be highly desirable if the flue gas mixtures can be used for CO<sub>2</sub> conversion but without pre-separation of CO<sub>2</sub>. Based on our research, there appears to be a unique advantage of directly using flue gases, rather than pre-separated and purified CO<sub>2</sub> from flue gases, for the proposed tri-reforming process.

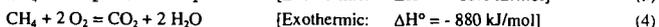
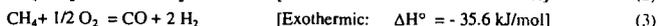
Typical flue gases from natural gas-fired power plants may contain 8-10% CO<sub>2</sub>, 18-20% H<sub>2</sub>O, 2-3% O<sub>2</sub>, and 67-72% N<sub>2</sub>; typical flue gases from coal-fired boilers may contain 12-14 vol% CO<sub>2</sub>, 8-10 vol% H<sub>2</sub>O, 3-5 vol % O<sub>2</sub> and 72-77% N<sub>2</sub> [Miller and Pisupati, 1999]. The typical furnace outlet temperature of flue gases is usually around 1200°C which will decrease gradually along the pathway of heat transfer, while the temperature of the flue gases going to stack is around 150°C [Miller and Pisupati, 1999]. Current toxic emission control technologies can remove the SO<sub>x</sub>, NO<sub>x</sub> and particulate matter effectively, but CO<sub>2</sub> and H<sub>2</sub>O as well as O<sub>2</sub> remain largely unchanged.

In the proposed tri-reforming process, CO<sub>2</sub> in the flue gas does not need to be separated. In fact, H<sub>2</sub>O and O<sub>2</sub> along with CO<sub>2</sub> in the waste flue gas from fossil-fuel-based power plants will be utilized for tri-reforming of natural gas for the production of synthesis gas.

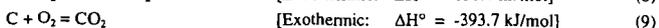
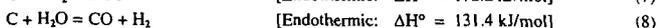
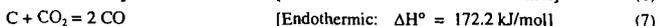
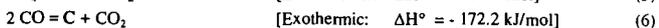
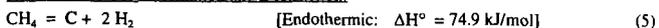
### PROPOSED TRI-REFORMING PROCESS

The tri-reforming refers to simultaneous oxy-CO<sub>2</sub>-steam reforming of natural gas (eqs. 1-4). It is a synergetic combination of endothermic CO<sub>2</sub> reforming (eq. 1) and steam reforming (eq. 2) and exothermic partial oxidation of methane (eqs. 3 and 4).

#### Tri-reforming of Natural Gas:



#### Reactions for Coke Formation and Destruction:



The tri-reforming (Figure 1) is an innovative approach to CO<sub>2</sub> conversion using flue gases for syngas production. Coupling CO<sub>2</sub> reforming and steam reforming can give syngas with desired H<sub>2</sub>/CO ratios for methanol (MeOH) and Fischer-Tropsch (F-T) synthesis. Steam reforming is widely used in industry for making H<sub>2</sub> and syngas [Rostrup-Nielson, 1993; Armor, 1999; Gunardson and Abrardo, 1999]. When CO-rich syngas for oxo synthesis and syngas with H<sub>2</sub>/CO ratio of 2 are needed for F-T synthesis and methanol synthesis, steam reforming alone can not give the desired H<sub>2</sub>/CO ratio [Gunardson, 1998]. Steam reforming gives too high a H<sub>2</sub>/CO ratio ( $\geq 3$ ) and thus need to import CO<sub>2</sub> for making syngas with H<sub>2</sub>/CO ratios of 2 or lower.

CO<sub>2</sub> reforming (dry reforming) of CH<sub>4</sub> has attracted considerable attention worldwide [Ashcroft et al., 1991; Rostrup-Nielson et al., 1993], and the research up to 1998 has been reviewed [Bradford and Vannice, 1998]. A simple estimate of energetics indicates that CO<sub>2</sub> reforming is 20% more endothermic than steam reforming (eq. 2 vs eq. 1), and so it does cost more energy. However, it can be done and is indeed necessary for adjusting H<sub>2</sub>/CO ratio for making MeOH or F-T synthesis gas. There are two industrial processes that utilizes this reaction, including SPARG [O'Connor and Ross, 1998; Gunardson, 1998] and Calcor [Teuner, 1987; Kurz and Teuner, 1990]. CO<sub>2</sub> reforming of methane suffers from a major problem of carbon formation (eqs. 5 and 6), particularly at elevated pressures [Song et al., 2000; Sinivasa et al., 2000]. When CO<sub>2</sub> reforming is coupled to steam reforming, this problem can be effectively mitigated. This carbon formation in CO<sub>2</sub> reforming can be reduced by the addition of oxygen.

Direct partial oxidation of CH<sub>4</sub> to produce syngas [Dissanayake et al., 1991; Hickman et al., 1993] and partial combustion of CH<sub>4</sub> for energy-efficient autothermal syngas production [Pena et al., 1996] are being explored. These reactions are important but the catalytic partial oxidation is more difficult to control. The major operating problems in catalytic partial oxidation are the over-heating or hot spot due to exothermic nature of the oxidation reactions, and consequently coupling the exothermic reaction with an endothermic reaction could solve this problem [Ruckenstein and Hu, 1998].

The combination of dry reforming with steam reforming can accomplish two important missions: to produce syngas with desired H<sub>2</sub>/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming. Integrating steam reforming and partial oxidation with CO<sub>2</sub> reforming could dramatically minimize or eliminate carbon formation on reforming catalyst thus increase catalyst life and process efficiency. Therefore, the proposed tri-reforming can solve two important problems that are encountered in individual processing. The incorporation of O<sub>2</sub> in the reaction generates heat in situ that can be used to increase energy efficiency and O<sub>2</sub> also reduces or eliminates the carbon formation on the reforming catalyst. The tri-reforming can thus be achieved with natural gas and flue gases using the 'waste heat' in the power plant and the heat generated in situ from oxidation with the O<sub>2</sub> that is already present in flue gas.

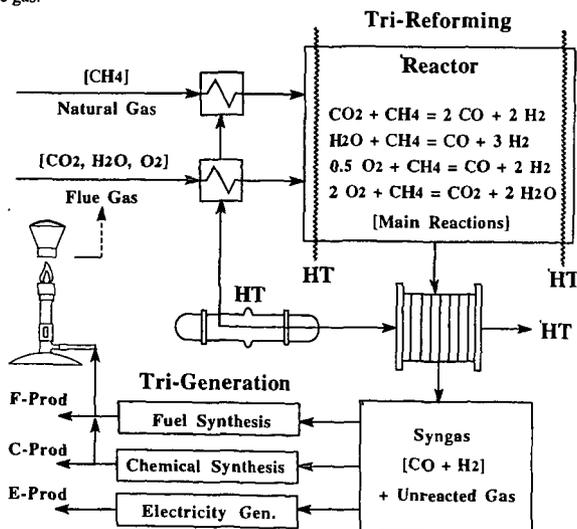


Figure 1. Conceptual design of proposed tri-reforming process in the recently proposed CO<sub>2</sub>-based tri-generation system (Version 2 in May 2000).

As illustrated in Figure 1, the tri-reforming is the key step in the recently proposed CO<sub>2</sub>-based tri-generation of fuels, chemicals, and electricity [Song, 1999, 2000]. In principle, once the syngas with desired H<sub>2</sub>/CO ratio is produced from tri-reforming, the syngas can be used to produce liquid fuels by established routes such as Fischer-Tropsch synthesis, and to manufacture industrial chemicals by methanol and oxo synthesis. Syngas can also be used for generating electricity either by IGCC type generators or by using fuel cells.

The proposed tri-reforming concept is consistent, in general, with the goals of Vision 21 EnergyPlex concept [DOE/FETC, 1999b, 1999c] being developed by the U.S. DOE. The goals of Vision 21 EnergyPlex (plants) include greater efficiency of power generation (>60% with coal, >75% with natural gas), greater overall thermal efficiency (85-90%), near zero-emissions of traditional pollutants, reduction of greenhouse gas (40-50% reduction in CO<sub>2</sub> emission), and coproduction of fuels [DOE/FE, 1999b].

The challenges and feasibility issues and related literature information have been discussed recently [Song, 1999, 2000]. Current flue gases contain inert N<sub>2</sub> gas in high concentrations, and thus the conversion process design requires the considerations on how to dispose inert gas. It is possible that oxygen-enriched air or oxygen will be used in power plants in the future. If that becomes a reality, then the proposed tri-reforming process will be even more attractive because of much lower inert gas concentration and thus higher system efficiency. Another challenge is how to deal with the small amounts of NO<sub>x</sub>, SO<sub>x</sub> and other toxic substances that are present in most flue gases.

### IS TRI-REFORMING FEASIBLE?

We have not found any previous publications or reports on reforming using flue gases or CO<sub>2</sub> conversion using flue gases related to the proposed concept [Song, 1999, 2000]. Our computational thermodynamic analysis shows there are benefits of incorporating steam (H<sub>2</sub>O) and oxygen (O<sub>2</sub>) simultaneous in CO<sub>2</sub> reforming of natural gas or CH<sub>4</sub> [Pan et al., 1999; Pan and Song, 2000]. On the other hand, some recent laboratory studies with pure gases have shown that the addition of oxygen to CO<sub>2</sub> reforming [Vernon et al., 1992; Choudhary et al., 1995; O'Connor and Ross, 1998; Ruckenstein and Hu, 1998] or the addition of oxygen to steam reforming of CH<sub>4</sub> [Choudhary et al., 1998] can have some beneficial effects in terms of improved energy efficiency or synergetic effects in processing and in mitigation of coking. A feasibility analysis by calculation showed that utilizing CO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/CH<sub>4</sub> for making synthesis gas is feasible [Tjajopoulos and Vasalos, 1998]. Inui and coworkers have studied energy-efficient H<sub>2</sub> production by using mixture of pure gases including CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> [Inui et al., 1995]. Choudhary and coworkers have reported on their laboratory experimental study on simultaneous steam and CO<sub>2</sub> reforming of methane over Ni/MgO-SA in the presence of O<sub>2</sub> at atmospheric pressure; they have shown that it is possible to convert methane into syngas with high conversion and high selectivity for both CO and H<sub>2</sub> [Choudhary et al., 1998]. Ross and coworkers have shown that a Pt/ZrO<sub>2</sub> catalyst is active for steam and CO<sub>2</sub> reforming combined with partial oxidation of methane [Hegarty et al., 1998]. Therefore, the proposed tri-reforming of flue gas from power plants appears to be feasible and safe, although its demonstration requires detailed experimental studies, computational analysis as well as engineering evaluations.

### CONCLUDING REMARKS

A new process concept, tri-reforming, is proposed for effective conversion and utilization of CO<sub>2</sub> in the waste flue gases from fossil fuel-based power plants in the 21st century. The CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> in the flue gas need not be pre-separated because they will be used as co-reactants for the tri-reforming of natural gas. In the tri-reforming (simultaneous oxy-CO<sub>2</sub>-steam reforming) process, the flue gas and natural gas are used as chemical feedstock for production of synthesis gas (CO+H<sub>2</sub>) with desired H<sub>2</sub>/CO ratios.

The proposed tri-reforming is a synergetic combination of CO<sub>2</sub> reforming, steam reforming, and partial oxidation of natural gas. The tri-reforming process solves some of the major problems in CO<sub>2</sub> reforming, in steam reforming, and in partial oxidation. It also makes use of the 'waste heat' in the power plant and heat generated in situ from oxidation with the O<sub>2</sub> that is already present in flue gas. This tri-reforming process could be applied, in principle, for natural gas-based or coal-based power plants and IGCC power plants.

Another important feature of the proposed tri-reforming is that this is the first innovative approach to conversion and utilization of CO<sub>2</sub> in flue gases from power plants without CO<sub>2</sub> separation. Many

questions remain to be answered, and further research is needed in order to establish and demonstrate this new process concept.

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