

PERP Program – Coal to Olefins New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, *Coal to Olefins (05/06S5)*. To view the table of contents or order this report, please click on the link here: <u>http://www.chemsystems.com/reports/index.cfm?catID=2</u> and scroll down.

INTRODUCTION

In the leading industrial nations, the demand for chemical feedstocks is mainly satisfied by oil and thus by a feedstock that will no longer be sufficiently available in a few decades. Coal is an alternative source for chemical feedstocks, the reserves being sufficient for several centuries. China is already taking advantage of their immense coal resource and has recently announced several coal-to-olefins (CTO) projects.

- Duolun project of Datang International Power Generation Co. Ltd.
- Baotou Shenhua Coal Chemical Co., Ltd.
- Shenhua Ningxia Coal Industry Group Co., Ltd.
- Shaanxi Xinxing Coal Olefin Co., Ltd.

These projects are expected to start-up between the end of 2008 to 2010. In order to decrease the risk of investment in coal-to-olefins, other projects will not be approved by the Chinese National Development and Reform Commission (NDRC) until the above four industrial units are operated successfully in 2009-2010.

TECHNOLOGY ROUTES

This report examines the technology routes and economics for coal-to-olefins. In summary, there are two distinct routes for the conversion of coal to chemicals, as summarized in Figure 1. This report will concentrate on the coal to syngas to dimethyl ether (DME)/methanol to olefins route.

COAL TO CHEMICALS ISSUES

In general, coal gasification technologies are mature and primarily it is economic issues that have delayed full scale implementation. U.S. government agencies such as DOE/NETL have directed their efforts in the area of gasification towards electricity generation and to a lesser degree to the production of transportation fuels, such as diesel, and not to the production of commodity chemicals. In manufacturing chemicals, there are technical issues that need to be addressed:



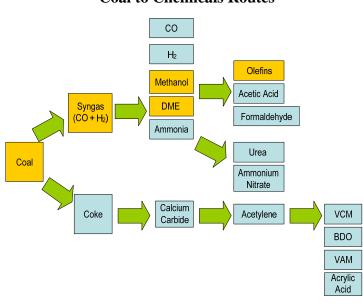


Figure 1 Coal to Chemicals Routes

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- Coal type affects the efficiencies and economics of gasification.
- Minor impurities which do not impact power generation, may affect chemical manufacture.
- Control systems that can handle changes in syngas composition due to changes in feedstock composition or end product requirements needs to be further developed.
- The economics of Fischer-Tropsch technology depend on the product(s) desired and the hydrogen to carbon ratio of the syngas, which is not necessarily the same for fuels and chemicals.
- Environmental consideration such as CO₂ sequestration and handling of wastes (e.g., heavy metals) will influence the economics of gasification.
- Co-firing multiple feedstocks (e.g., coal and biomass) needs to be further developed.



CHEMICALS FROM SYNGAS

Methanol

The main options with respect to reformer configuration are described below. The terminology can vary between licensors. The conventional process employs a steam reformer with catalyst packed in tubes (SMR or Steam Methane Reformer).

In the combined reformer or two-step reforming process, the tubular reformer is combined in series with a secondary reformer to which oxygen is added. Compared to the conventional process, the combined reformer process requires additional capital in terms of an Air Separation Unit (ASU) and the secondary reformer, plus associated items. However, capital cost advantages are gained from a smaller primary reformer, smaller equipment in the syngas system, and a smaller syngas compressor. In Nexant's experience, the capital costs and the total natural gas usage of the conventional and the combined reformer systems are broadly similar.

Some licensors offer a system with a single stage autothermal reformer based on oxygen addition. The syngas is deficient in hydrogen compared to the ideal molar ratio. This can be remedied if hydrogen is available, such as from an existing conventional reformer system. The advantages cited for a single autothermal reformer include reduced capital cost because the system is simpler than a combined reformer system. In addition, the reactor may be operated at high pressures, potentially removing the need for the main syngas compressor. In practice, technical constraints such as materials of construction prevent operation at the required pressure; however, the compressor can be significantly offloaded. The steam to carbon ratio can be lower than with the conventional SMR; a ratio of 0.6 on an industrial scale is quoted.

The gas heated reformer system dispenses with a fired primary reformer. Instead, the hot gases from the secondary oxygen-blown secondary reformer are used to provide indirect heat to an unfired primary reformer. The advantages are claimed to include the benefits of combined reforming, plus improved thermal efficiency resulting from direct use of hot gases rather than by conversion to steam.

Other options include the use of an adiabatic catalytic pre-reformer which eases the duty for the main reformer by degrading heavier hydrocarbons to methane, carbon oxides, and hydrogen. The operating duty on the reformer is significantly reduced as is the risk of coking.

The synthesis reactor, or converter, may be of several forms. One of the differentiating factors is the method of moderating the reaction. One technique is the injection of shots of syngas at various positions, the quench system. In another type of converter, steam is raised, often from a shell and tube configuration, and is usually used as process steam for the reformer. Two stage converter systems are available, and are particularly useful in reducing equipment sizes at very large capacities. In the Lurgi system, the first converter operates at high space velocities and is used to generate steam while the second reactor has indirect gas-cooling to control the temperature profile to



close to optimum. High conversion in the two stage converter system results in considerably reduced syngas recycle.

One Synergy has developed a novel methanol synthesis loop configuration (patent pending), particularly suited to large capacity plants. This scheme utilizes two methanol converters (each generating medium pressure steam) in series and provides benefits over a conventional arrangement in terms of reduced catalyst volume. Compared to a conventional large capacity methanol synthesis loop with parallel converters, the series loop operates with approximately 30 percent lower recycle ratio. This is beneficial in terms of reducing piping size and maximizing circulator capacity. However, since the gas is circulated through the converters in series, the mass flux through each converter is actually increased compared to a parallel converter layout. This has the benefit of maximizing the reaction rate per unit volume, reducing catalyst volumes and improving the heat transfer performance, providing better temperature control resulting in lower temperatures and therefore longer catalyst life. The series loop configuration is best suited to larger plants, where two or more converters operating in parallel would be required to meet the desired capacity. The full benefit of the series configuration can only be realized if product is separated after each converter. This ensures that equilibrium limitations do not come into play and reaction rates are maximized in each converter, thereby minimizing the catalyst volume required.

Gas flow differs between proprietary offerings. The ARC converter (JM Catalysts/Methanol Casale) is a quench type converter, but with separate catalyst beds rather than a continuous bed to improve distribution. Single streams of up to 3,000 tons per day are regarded as feasible by JM Catalysts. One Synergy also offers the Steam Raising converter (SRC) with catalyst contained on the shell side and steam in the tubes. The gas flows radially out through the catalyst bed from the inside to the outside. Radial flow reactors such as the SRC, Toyo MRF-Z, and DPT's proprietary design offer low pressure drops, and can be scaled up to very large sizes by extending the height. Radial flow reactors can be combined with steam raising.

Olefins

There are two types of methanol-to-olefins processes commercially available. The first is the UOP/HYDRO Methanol to Olefins (MTO) process, which produces propylene and ethylene with minimal or no C_5 + co-product. The second is Lurgi's "methanol-to-propylene (MTP)" process, which produces propylene and gasoline. In addition ExxonMobil had done significant research in this area.

More recently Dalian Institute of Chemical Physics (DICP) has done some work in this area and is close to commercializing its own technology.



Syngas via Dimethyl Ether to Olefins Process (SDTO)

In the mid-1990s, DICP was awarded two patents in the United States concerned with the conversion of methanol/dimethyl ether (DME) to light olefins. These patents are the basis for the syngas via dimethyl ether to olefin process (SDTO). Compared with the MTO process, SDTO directly converts synthesis gas to DME with high carbon monoxide conversion, thus exhibiting greater efficiency than the MTO process. Other special features of the SDTO process include:

- Bifunctional metal (Cu, Zn, etc.)-zeolite catalysts have been developed, which can convert syngas very selectively to DME with high carbon monoxide (CO) conversion (this reaction is far more favorable thermodynamically than methanol synthesis from syngas).
- The development of a silicoaluminophosphate type molecular sieve catalyst, SAPO-34, for the conversion of DME to lower olefins with ethylene selectivity as high as 50-60 percent, which is higher than ZSM-5 type zeolites can achieve.
- A fluid-bed reactor is utilized in the second stage for the conversion of DME to lower olefins and no water addition is needed during the reaction, while maintaining continuous operation.
- Syngas to DME breaks the thermodynamic limit of syngas to methanol system with up to over 90 percent CO conversion, 5-8 percent investment savings and 5 percent operational cost savings.
- Ethylene selectivity improvement of 50-60 percent by using the small pore molecular sieve catalyst of silicon-aluminum phosphate(SAPO-34).

ECONOMICS

The economics of the coal-to-olefins (CTO) plants have been prepared for both the USGC and China and in each case compared with the production costs for ethylene from conventional technology. The CTO economics are based on a single methanol synthesis unit with multiple upstream coal gasification trains (including a spare) and one or more downstream methanol-to-olefin units. The economics have been examined for methanol capacities of 2,500, 5,000 and 7,500 tons per day.

For the U.S. the cost of production (including depreciation and return) increase significantly at the smaller capacity such that the CTO route is simply not competitive with conventional technology. At the larger capacity, the CTO route is competitive and, in fact shows a small advantage over the conventional ethane-based technology. The higher investment for two MTO trains producing 500 kta of ethylene (total) results in higher capital charges when compared to the smaller plants. If the single train capacity of the MTO unit would be increased to better match the methanol facility, even lower costs for the ethylene could be expected.



The Chinese CTO cases show a decided advantage at large scales as compared to conventional steam cracking. Two factors drive this cost advantage: low coal costs and relatively high propylene byproduct credit due to an unusually high propylene prices. This cost advantage is consistent with the recent burst of activity in CTO projects in China.

COMMERCIAL ANALYSIS

Supply/demand forecasts out to 2010 for ethylene for the United States, Western Europe, and Asia Pacific are also provided in the report.

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