

MAR 16 1981

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DOE/PC/30276--T1

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DE84 004064

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DOE Grant No. DE-FG-2280PC30276

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## Evaluation of the Slurry Methanol Reactor

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### Introduction

The following report deals with an evaluation of the slurry methanol process under development by Chem Systems (Ref. 1), and its potential value for production of methanol from coal. This process has received considerable attention and a large pilot plant is under construction with DOE support.

The Chem Systems slurry process is a three phase reactor in which catalyst is suspended in a nonactive liquid, which mainly acts as a heat transfer medium. The reactor is similar to the slurry reactor for Fischer Tropsch processes described by Koelbel (2). It allows very good temperature control, and continuous catalyst addition and removal. If the liquid is a solvent for methanol, it also allows higher conversions of the gas as the methanol is preferentially removed from the gas inside the reactor, and can be flashed from the solvent.

Parson (3) has published the summary of an economic evaluation, in which it is claimed that the reactor has an advantage over the ICI methanol process. No details of the comparison have been published as it is based on confidential data. Comparing the slurry reactor for methanol solely to the ICI reactor is not a fair comparison. The ICI reactor was developed for plants producing methanol from natural gas. It was also developed at a time when energy was cheap and the main criterion was cheaper construction costs.

The ICI reactor could be modified to fit the special demands of a methanol from coal plant<sup>(4)</sup>. Looking at available reactors, the Lurgi reactor<sup>(7)</sup>, which has a high heat recovery, is a more

appropriate comparison. We therefore have to look at the inherent advantages and disadvantages of the different reactors and try to understand how different design goals would be achieved.

What I will try to do here is to evaluate the inherent advantages and disadvantages of a slurry reactor for methanol production and the results should be valuable for other reaction systems for which a slurry reactor is considered.

## II. Advantages and disadvantages of the slurry reactor

Let me start with a short discussion of the inherent advantages and disadvantages of the slurry reactor, and the potential reasons for developing it. We here have to compare it both to a fixed and fluid bed reactor.

### a) Advantages

#### 1) Temperature control and heat recovery

The slurry reactor has excellent temperature control and allows good heat recovery. It shares this advantage with a fluid bed, but the control is claimed to be slightly better in a slurry reactor. This is probably true for fast reactions as the mass transfer resistance in the slurry reactor prevents local high reaction rates, but this is not an important consideration in methanol, as the temperature control available in a fixed or fluid bed is sufficient.

#### 2) Preferential removal of products from the gas

If the liquid in the slurry reactor is a good solvent for methanol, the dissolved methanol can be continuously removed by flashing the solvent at reduced pressure. This will increase the methanol conversion per pass of synthesis gas. Methanol conversion of the synthesis gas is limited by equilibrium constraints to 30-50% per pass and recycle of unconverted gas is therefore required for high conversion. Removal of methanol by dissolving it theoretically allows complete

conversion, but practically, conversion is still limited as complete conversion would need very high recycle through the flash separation unit. Furthermore, the solvent also dissolves syngas. The reaction actually depends on the fact that the syngas has a reasonable concentration in the liquid and in an ebullated bed reactor this concentration will approach equilibrium in the space above the catalyst. Furthermore, any dissolved syngas that escapes in the flash separation unit has to be recompressed, which is a significant penalty. There is therefore an optimum recycle rate for every solvent, and the potential increase in conversion compared to equilibrium is not very large.

3) Catalyst replacement, regeneration and attrition

The slurry reactor shares with the fluid bed the advantage of allowing continuous replacement and regeneration of the catalyst. This is not of importance in the standard methanol reaction, but could be of importance if reaction conditions are changed such that coke is formed, or catalyst life reduced. We will discuss the implication of this advantage later. Its main advantage over a fluid bed is that it has lower requirements on the strength and attrition resistance of the catalyst. This is the decisive advantage a slurry reactor has for certain Fischer Tropsch processes. The fluid bed FT process requires a high  $H_2/CO$  ratio. Low hydrogen to CO ratio promotes coke formation in an iron catalyst, and the coke formed causes the iron catalyst particles to disintegrate. The slurry not only reduces attrition but also allows retainment of very fine particles in the slurry. It therefore has an advantage for Fischer Tropsch if the syngas has a low  $H_2/CO$  ratio.

4) Ability to handle an evaporating liquid feed

Both a slurry reactor and a fluid bed can handle directly liquid feeds that evaporate by boiling. In fixed beds this can lead to shattering of catalyst particles. For methanol this has one potential advantage. Syngas from many second generation gasifiers (6,10)

have a low  $H_2/CO$  ratio which yield higher thermal efficiencies. In a methanol reactor we require a syngas of 2:1 at least. Methanol catalysts are shift catalysts. By adding water to the reactor we could use the reaction heat to generate the steam for the shift, thereby saving both the shift reactor and part of the steam boiler. This reduces the heat transfer requirements inside the reactor. As the  $H_2$  is continuously removed by the reaction we also save the excess steam that is required in a shift reactor. We will discuss this later. Fixed bed reactors can achieve this if the reactors are staged and water is introduced in a special quench section between the stages.

#### 5) Size

It is claimed that a slurry reactor can be built at a larger size as compared to a packed bed reactor. There is no real experience to back this claim. As we deal here with a reactor at 700 psi, there is a limit to reactor size. This claim is doubtful in another way. As we will show in the next section a slurry reactor requires about a 5-10 times larger reactor volume which eliminates all potential advantages of scale. In fact the number of slurry reactors required for the same production capacity is larger than for fixed bed reactors.

#### Disadvantages

#### 6) Lower volumetric space velocity and mass transfer resistances

In a three phase system with dispersed catalyst, there is considerable resistance to mass transfer as the gas reaction occurs at the solid surface and the liquid is not involved in the reaction. Furthermore, to provide good contact we have to limit the solids loading. The German FT process operated with a volumetric solid loading of less than 10% based on volume, versus the customary 60% in a fixed bed reactor and 30% in a fluid bed reactor. The reason the German FT reactor is designed at low catalyst loading is to achieve high catalyst utilization in the presence of gas liquid mass transfer resistance.

For a fixed bed this translates for a methanol catalyst to a catalyst loading of 70 lb/ft<sup>3</sup>. A fluid bed would have about 60% of this density whereas in a slurry reactor the catalyst loading would be lower by a factor of 10. In Ref. (1) higher catalyst loadings were used (from 15-25 lb/ft<sup>3</sup>) but in that case, the catalyst efficiency decreases as the reaction becomes mass transfer controlled, unless the reaction itself is very slow. Despite the higher density the reactor volume in Ref. 1 is about 5-10 times larger as compared to a packed bed reactor. This is a significant penalty and slurry reactors are only used if the potential advantages mentioned before are significant, and there is therefore a strong driving force for use of a slurry reactor. This is true, for example, for a slurry FT reactor as it is the only reactor that can at present directly convert a low H<sub>2</sub>/CO gas under the reaction conditions used, using an iron catalyst.

7) Difficult scaleup

As there is little experience with very large slurry catalytic gas phase reactors, scaleup is more difficult than for fixed bed reactors and a large pilot plant is required. This difficulty could probably be minimized by proper design. The only really large slurry reactor known to the writer is the H-oil reactor and this is a significantly different case, such that the experience from it cannot be directly translated to our case. In H-oil gas conversion is low and recycle is high and there is no advantage to plug flow, whereas such an advantage clearly exists in our case.

8) Solvent consumption

The stability of the solvent for long times has to be established, and to reduce solvent losses vapor pressure and entrainment have to be minimized. Establishing the stability of the solvent requires long runs in the pilot plant.

### III. Economic evaluation of the advantages and disadvantages of the slurry reactor

Let us look at the implication of each of the advantages and disadvantages. But before going into that, we need some basis of reference to estimate the importance of different savings. First of all, if we deal with coal we have to realize one difference compared to natural gas. In a methanol plant from natural gas, the methanol synthesis section itself is 40% of the total plant investment. In coal it is about 10% (Ref. 3,5). The reason for the difference is that the syngas preparation section is more expensive in a coal plant. Furthermore, the reactors themselves comprise only 35% of the cost of this section. The rest is for the compressor heat, exchangers, and condenser. A 20% savings in the methanol conversion section translates into a 2% savings for the total plant. To achieve any real effect, our reactor has to affect the total flow sheet. The advantage of the FT slurry reactor (6) is that it saves the steam for shift and eliminates the need for a shift reactor. This advantage by far outweighs the higher cost of the slurry reactor. In a similar vein the Lurgi methanol reactor, which is basically a tubular heat exchanger, with catalyst in the tubes, cooled by steam generation on the outside, is a more expensive reactor than the ICI design which is a shot-cooled multistage packed bed reactor. It gains its advantage mainly from the better heat recovery and its ability to produce 600 psi steam, which improves the thermal efficiency of the total process.

Any significant advantage for one reactor design over another will have to come, not from a cheaper reactor design, but from the effect on the total flow sheet. This will be therefore the emphasis of our analysis. Let us now look specifically at the implication of each of the advantages and disadvantages for methanol.

1). Temperature control and heat recovery

In methanol close temperature control is not a very important factor. In the slurry FT there is a very narrow temperature window in which we can operate and the closer the temperature control, the better the selectivity. Here, the temperature window is about 50°F, the outlet temperature is controlled by the equilibrium constraints and is about 500°F. At 600°F we start to damage the catalyst. Very close temperature control all through the reactor has limited value, and a 30-40°F range is sufficient, and obtainable in suitably designed packed bed reactors. The reason for this is that the methanol reaction is reasonably slow at the temperatures used, and equilibrium limited at high temperatures. A tubular reactor with cooling is able to control the reaction within the required limits, so is a multistage bed with intermediate cooling. Unlike the FT case, there is no significant advantage to the better temperature control that either a fluid bed or a fixed bed offers. It is true that the ICI reactor operates with a larger recycle, (5:1), but this can be modified by better design, and a slurry reactor has the same recycle requirements as a well-designed packed bed reactor. The only way to reduce recycle would be by using a liquid which is a good solvent for methanol. If the recycle is not reduced, then the slurry reactor has no advantage in terms of heat recovery over a properly designed packed bed reactor. Shot-cooled reactors, such as the ICI design, recover a large part of the reaction heat as low quality heat. In the standard design of present methanol plants from natural gas, this heat is used to preheat the boiler water for the waste heat boiler of the steam reformer. Syngas plants from coal have low quality heat available from other sources and cannot efficiently use the low quality heat from the methanol reactor. There is therefore an advantage to generate medium quality steam (600 psi). This can be done in any packed bed reactor with direct steam generation



by heat exchangers in the reactor itself. Lurgi achieves 80% recovery of the reaction heat as 600 psi steam. Similar results have been achieved by Mitsubishi (8) which uses a multiple bed reactor with immediate cooling by steam generation. Haldor Topso is also promoting a similar design.

It is hard to improve on these designs. The increased heat recovery by any method increases reactor cost. The increase is, however, negligible as compared to total plant cost in a coal plant. It is also much cheaper than a coal boiler generating the same amount of steam. On the other hand, there was little justification for such an expense in a natural gas methanol plant, as enough steam is generated in the waste heat boiler of the steam reformer.

Here, we have a typical example of what happens when we compare a proposed process to an existing process by standard cost analysis. We may observe an advantage for the new process which could be far easier achieved by modifying the old process. We therefore have to try to understand why the present process was designed the way it is and what it would cost to modify it.

In terms of heat recovery therefore the proper yardstick for comparison is a Lurgi methanol reactor, though an ICI reactor could probably be modified to give similar results. In summary, compared to the Lurgi reactor a slurry methanol reactor does not seem to have any real advantage in terms of heat recovery. A properly designed packed bed reactor can recover steam at 600 psi and 80% recovery, which is better than the Parson design for the Chem Systems reactor (285 psi), though a properly designed slurry reactor has the same capability for steam recovery as a packed bed.

2) Reduced recycle by selective removal of methanol

Despite the fact that there are no good data for any methanol reactor operating with a solvent to achieve a significantly reduced

recycle, we can estimate the advantage of preferentially dissolving methanol.

Assume we could reduce recycle by a factor of two from 2:1 to one to one, which is a very optimistic assumption. What would we save? We would save part of the heat exchanger and condenser cost. The heat exchanger surface would be reduced by a factor significantly less than 2. We now have to treat and cool 2 lbs. of total feed for every pound of methanol instead of three. We still have to condense the same amount of methanol.

So at best our heat exchanger cost for feed preheat and cooling would be reduced by 30%. If we assume our total heat exchange surface to be reduced to approximately 80% of the base case, we would have a saving of at best 15%, in investment for heat exchange. As our total heat exchanger cost is about 30%, we end up with a potential savings of 5% for this section to be balanced by the larger reactor cost for the slurry reactor.

The incremental amount of heat recovered by the lower recycle is also small. We now have a total feed of 2 lbs. for each pound of product instead of 3 lbs. A savings of one lb. of feed is equivalent to a gain in heat recovery of about 100 BTU/lb, or less than 6% of the reaction heat. However, we would lose energy in recompressing the dissolved gas, and this penalty could either eliminate or reduce our savings.

The fact that reduced recycle has no larger advantage is due here to two factors. The recycle required in a coal-to-methanol plant is significantly lower than in a methane-to-methanol plant due to the lower  $H_2/CO$  ratio. Thus, the potential for savings is a priori small. Furthermore, methanol is easy to remove from the recycle by condensation. In processes which require separation processes, such as absorption, there is a much greater advantage for reducing recycle.

Slurry reactors have one advantage in terms of heat transfer. The heat exchanger in the reactor itself is significantly smaller due to the better heat transfer coefficient in the liquid. We deal with this in the section on reactor cost.

Another advantage of the slurry reactor is the lower pressure drop. This is quite small as normally half the pressure drop occurs in the heat exchangers and the feed systems. Reduced recycle by selective methanol removal in a solvent would have, here, an additional advantage as the smaller recycle saves compression. This has to be weighed against the compression requirements for the dissolved syngas released from flashing the dissolved methanol.

### 3) Catalyst replacement regeneration and utilization

The standard methanol catalyst has a long life if temperature is closely controlled. In a standard methanol reactor there is no need for continuous replacement or regeneration. For a slurry reactor to have any real advantage overcoming its inherent disadvantages, we need a process that can utilize this property in a beneficial way.

The only case where this is a real advantage, of which this writer is aware, is operation of the reactor with a low  $H_2/CO$  ratio syngas as feed.

Methanol requires stoichiometrically a feed with a  $H_2/CO$  ratio of 2. In practice this ratio is increased to slightly above 2 (up to 2.5) and  $CO_2$  is added to achieve high conversion. The increased ratio is for two reasons. The  $CO_2$  and the water formed increase the reaction rate. Second, the higher  $H_2/CO$  ratio protects the catalyst. There are, however, no published data as to the behavior of low methanol catalysts with low  $H_2/CO$  ratio syngas. We can only speculate from the behavior of FT catalysts that high CO concentrations lead to coke formation via the Boudouart reaction



We also do not know how the catalyst itself is affected by high CO concentrations.

As long as we operate with a syngas with a concentration of 2:1, the advantage of eliminating a small excess of hydrogen is negligible. But if we want to utilize directly a syngas with a concentration of 0.5:1 to 0.9:1 as obtained in efficient gasifiers, the ability to handle a high CO concentration would be useful. There are two cases where this is of interest.

The first is the case where a methanol reactor is integrated into a combined cycle power plant using a medium BTU coal gasifier power plant to utilize the syngas capacity at lower load ratios. Here, the need to shift and the steam required for shift provide a penalty.

Without shift we can obtain about 30% conversion of a syngas with a  $H_2/CO$  ratio of 0.7:1. However, if we inject water into the reactor and shift the gas inside the reactor, the conversion can be increased to 60%. This could allow adjustment of the conversion in a power plant operation according to need with minimum penalty on thermal efficiency.

If high conversion of the syngas is required, then in addition to adding steam, we have to remove  $CO_2$  from the syngas as excess  $CO_2$  which will limit the shift reaction. We can achieve this by removing  $CO_2$  from the recycle or staging the reactors and removing the  $CO_2$  between the stages. In a large plant there is no penalty for using a staged reactor instead of recycle. In fact, there is an advantage in the case of methanol. Passing the total recycle through the  $CO_2$  adsorber is expensive, but here unnecessary. If we want to use a single reactor, we can recycle part of the unconverted gas through a  $CO_2$  adsorber and recycle the rest of the gas directly. Actual recycle rates and conversion depend on catalyst space velocity and feed

condition. What we did is to perform a few simulations to show that such operation is feasible. One example is given in Table 1.

The steam requirement for shift is here practically stoichiometric, whereas external shift prior to the reactor requires between 100-150% excess steam. This translates to a savings of 70 lb-100 lb steam per million BTU methanol produced.

The reduction of steam requirement for shift is achieved here by removing the  $H_2$  formed due to shift in the methanol reaction. This allows high steam conversion and eliminates the need for steam excess in this section. In a slurry reactor we can feed the water instead of steam. This reduces further the total steam requirement. We therefore have an energy savings equivalent to the energy value of 70 to 100 lbs. of steam, which for external shift, are required at 500 (or 800) psi and 500°F or we save about 70,000-100,000 BTU of coal per million BTU produced. We also save the investment required to generate 150-200 lbs of steam per day for each million BTU daily capacity.

The savings in coal are especially important though their present effect on cost is small. The savings due to an investment eliminating the investment for the shift reactor would be between \$100-\$200 per million BTU daily capacity, and the investment savings in steam generation is also about \$300-\$400 per million BTU product.

#### 4) Reactor cost

This should more than pay for the high cost of the slurry methanol reactor. We have no exact data on the incremental cost of the slurry reactor as no final design is available, but we can bound it. The total volume of the slurry reactor is about 1 ft<sup>3</sup>/million BTU product daily capacity. The reactor is simple and the heat exchange rate is higher than in a packed bed reactor. Overall there should be an increase in investment cost compared to a packed bed reactor, but it should be small and less than \$100 per million BTU daily capacity.

We therefore end up with a net potential savings of about \$300-\$400 per million BTU product or about 6-8% of total investment. The savings are mainly due to the reduction in boiler capacity.

The design reported in Ref. 3 has two disadvantages that might be improved by design and further development. One is the lower steam quality which could be improved by placing the heat exchanger in the reactor. The second is low catalyst efficiency, which requires much higher catalyst loading (3-4 times higher) and consumption. While a larger reactor volume is necessitated by the mass transfer resistance of the slurry reactor, the same is not necessarily true for the catalyst itself. One can reduce catalyst requirement by decreasing both catalyst size and loading. Smaller catalyst particles will minimize diffusion resistance in the liquid phase. There is an optimum catalyst loading as at high catalyst loading the mass transfer from the gas phase into the liquid phase decreases due to lower holdup of the gas. The amount of catalyst required is also determined by the mass transfer from the gas phase to the liquid. The Koelbel reactor had low volumetric throughput but high conversion rates per unit of catalyst.

It is not clear that part of the advantage of the slurry reactor could not be achieved in a fixed bed by developing a suitable catalyst. As most of the knowhow is proprietary we have no way of judging this potential. The main problem here is the ability of the catalyst to operate with a low  $H_2/CO$  ratio. On the other hand such a reactor would not be able to handle direct water injection and therefore the slurry reactor might still have some advantage. In fixed bed reactors this would require staging with intermediate water quench, and we do not have sufficient data for a comparison of this case.

Summary

In the preceding we tried to evaluate the potential advantage of a slurry reactor for methanol production. The conclusion derived is that the slurry reactor has higher investment cost due to the low volumetric space velocity. Reactor volume will be about 5-10 times larger than in a standard packed bed.

If the syngas has a sufficient  $H_2/CO$  ratio then the use of the slurry reactor has no advantage that will compensate for the inherently higher cost.

On the other hand, if the hydrogen content of the syngas is low (0.5:1 to 1.2:1) as in most advanced gasifiers, then the slurry reactor has the potential to eliminate the external shift and reduce steam requirements. This property could lead to significant savings in this case. There is a possibility that with a proper catalyst similar results of integrating the shift into the reactor could be achieved in a fixed bed reactor. Even then the slurry reactor would have the advantage of being able to use water instead of steam. It might therefore be advisable that development of a slurry reactor for methanol should focus on converting syngas with a low  $H_2/CO$  ratio without prior shift by water injection into the reactor.

### References

1. AF-693, Liquid Phase Methanol, prepared by Chem Systems Inc., 1978.
2. Koelbel, H., Hammer, H. and Langemann, H., Chemiker Ztg, Chem Appir 92, p. 581 (1968).
3. Chow, T.K., et al., Fluor Engr. "Economic Studies of Coal Gasification Combined Cycle Systems for Electric Power Generation," EPRI report AF-692, Jan. 1978.
4. Pinto, A., "Optimizing the ICI Low Pressure Methanol Process," Chem. Eng., July 4, 1977, p. 102.
5. Schreiner, M., et al., "Research Guidance Studies to Assess Gasoline from Coal by Methanol to Gasoline and SASOL Type FT Technologies," Mobil Res. & Devel., FE-2447-13, Aug. 1978.
6. Chang, C.D., and Silvestri, A.J., "The Conversion of Methanol and other O Compounds to Hydrocarbon over Catalyst," J. Catalysis, 47, 249 (1977).
7. Miller, H. and Marschner, F., "Lurgi Makes Low Pressure Methanol," Hydrocarbon Processing, Sept. 1970.



Table 1

Methanol Reactor

Pressure 1300 psia      Temperature 540°F  
 Feed  $H_2/CO = 0.7$       Basis: 1 mole  $H_2$

Case 1 - No Recycle

Stage	$H_2/CO$ Feed	$CO+H_2$ % Cumulative	Conversion mole (cumulative)	Steam Requirements % (cumulative)	Steam Conversion %	Methanol moles
1	0.7	39.68	0.4831	99		0.3212
2	1.19	66.71	0.5277	98.96		0.5401
3	1.173	81.58	0.5713	98.96		0.6504
4	1.14	89.8	0.6	98.95		0.757

Case 2

Stage 1 Recycle 1:1  
 Stage 2 Recycle 2:1

1	0.7	61.19	0.57	98.93		0.4953
2	1.541	94.22	0.658	98.95		0.7627