# **Design and Control of a Methanol Reactor/Column Process**

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Methanol is one of the prime candidates for providing an alternative to petroleum-based liquid transportation fuels. It can be made from any renewable biomass hydrocarbon source by partial oxidation in an oxygenblown gasifier to produce synthesis gas, which is then converted into methanol. The purpose of this paper is to develop the economically optimum design of a methanol reactor/distillation column system with three gas recycle streams to produce high-purity methanol from synthesis gas. The economics consider capital costs, energy costs, the value of the methanol product, and the heating value of a vent stream that is necessary for purging off inert components entering in the feed. A plantwide control structure is developed that is capable of effectively handling large disturbances in the production rate and synthesis gas composition. The unique features of this control scheme are a lack of control of pressure in the reactor/recycle gas loop and a high-pressure override controller to handle stoichiometric imbalances in the composition of the synthesis gas feed.

# 1. Introduction

Global economic, environmental, and political forces have increased interest in developing sources of liquid transportation fuels that are not petroleum based. Renewable biomass has the potential to provide an alternative energy source that offers many long-term advantages over petroleum. Biomass can be converted into synthesis gas by gasification, and the synthesis gas can be efficiently converted into methanol using existing technology. It is possible that, in the not-to-distant future, most liquid consuming transportation vehicles (cars, trucks, trains, and planes) may use methanol as their energy source. Olah et al.<sup>1</sup> propose a "methanol economy" as a more practical approach compared to the widely discussed "hydrogen economy" because existing liquid fuel infrastructure (pipelines and tanks) could be used with little modification, and the safety concerns associated with hydrogen can be avoided.

This paper studies the process to convert synthesis gas into methanol. A cooled tubular reactor is used to react hydrogen with the carbon monoxide and carbon dioxide in the synthesis gas to produce methanol. Water is a byproduct. The gas-phase exothermic reactions are conducted in a packed tubular reactor, which is cooled by generating steam. A large gas recycle stream is required to obtain high overall conversion. A distillation column separates methanol from water.

A fixed amount of synthesis gas is fed into the system, and the effects of the many design optimization variables on the yield of methanol, the energy costs, and the capital costs are evaluated. These variables include reactor pressure, reactor size, concentration of inert components in the recycle gas, and pressure in a flash tank upstream of the column. The purpose of the flash tank is to keep light components from entering the column that would blanket the condenser.

The investigation reveals that the economics are dominated by methanol yield. Energy costs and capital costs are an order of magnitude smaller than the value of the product. The major energy cost is compression of the synthesis gas, so the optimum reactor operating pressure is a trade-off between compression costs and methanol yield. Reactor temperature is set such that high-pressure steam can be produced in the reactor. Reactor size is a trade-off between reactor and catalyst capital investment and recycle compression costs (energy and capital). Inert component concentration in the recycle gas is a trade-off between methanol yield (reactant losses in the vent) and compression costs. Selection of pressure in the flash tank is a trade-off between compressor costs in two compressors that are affected in opposite directions by varying the flash-tank pressure.

## 2. Process Studied

Figure 1 shows the flowsheet of the process. The equipment sizes and conditions shown are the economic optimum developed later in this paper. The Aspen "RK-Aspen" physical properties model is used in all units of the process except in the distillation column, in which the van Laar equations are used to calculate liquid activity coefficients.

**2.1. Compression and Reactor Preheating.** Synthesis gas at 51.2 bar is compressed in a two-stage compression system to 110 bar. The fresh feed is mostly hydrogen, carbon dioxide, and carbon monoxide, but it also contains small amounts of methane and nitrogen. The inert components must be purged out of the system. The two feed compressors consume a total of 8.98 MW of electric energy.

Three recycle gas streams are added, and the total gas stream enters a feed-effluent heat exchanger (FEHE) at 53 °C. The hot reactor effluent at 266 °C transfers 43.9 MW of heat into the cold stream, which heats it to 144 °C. The required area is 2157 m<sup>2</sup> using an overall heat-transfer coefficient of 144 kcal h<sup>-1</sup> m<sup>-2</sup> K<sup>-1</sup>. The gas is then heated to 150 °C in a reactor preheater (HX3) whose heat duty is 2.99 MW and uses medium-pressure steam (184 °C and 11 bar).

**2.2. Reactor.** The packed tubular reactor has 8000 tubes with length 12.2 m and diameter 0.03675 m. The reactor is cooled by generating high-pressure steam (254 °C and 42 bar), so the reactor temperatures through the tubes climb to a peak of about 280 °C. The reactor effluent is at 266 °C. The heat transfer rate is 28.3 MW using an overall heat-transfer coefficient of 244 kcal  $h^{-1} m^{-2} K^{-1}$ . The catalyst has a density of 2000 kg/m<sup>3</sup>, and the reactor void volume is 0.5. The reaction kinetics are discussed in a later section. The reasons for the selections of temperature, pressure, and reactor size are discussed later in this paper.

**2.3. Separator, Recycle, and Vent.** After the reactor effluent is cooled to 174 °C in the FEHE, it is further cooled to 38 °C

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Figure 1. Methanol flowsheet.

and partially condensed in a water-cooled heat exchanger whose heat duty is 102 MW. The stream is separated in a tank operating at 106.6 bar and 38 °C. The total pressure drop around the gas loop (heat exchangers and reactor) is 3.4 bar.

Most of the vapor stream is compressed back up to 110 bar and recycled. The recycle compressor work is 1.10 MW. The gas recycle flow rate is 38 465 kmol/h for the 11 450 kmol/h of synthesis gas feed (recycle-to-feed ratio = 3.36). A small fraction (0.022) is vented off at a flow rate of 865 kmol/h. This is where the inert methane and nitrogen in the synthesis gas fresh feed are removed from the system. The concentrations of methane and nitrogen in the vent and recycle streams are 28.5 and 4 mol %, respectively. These compositions should be compared with the 2.17 mol % methane and 0.3 mol % nitrogen in the fresh synthesis gas feed. The inerts are allowed to build up so that the losses of the reactants (hydrogen, carbon monoxide, and carbon dioxide) are kept small.

The hydrogen that is lost in the vent stream is 6.17% of the hydrogen in the synthesis gas feed. The carbon monoxide lost is 1.23% of the carbon dioxide in the synthesis gas feed. The carbon dioxide lost is 8.75%. The yield of methanol from the carbon monoxide and carbon dioxide in the synthesis gas feed is 96%.

**2.4. Flash and Distillation.** The liquid from the separator contains significant amounts of light components because of the high pressure in the separator. The concentration of hydrogen is 0.2 mol %. The concentration of methane is 1.2 mol %, and the concentration of carbon dioxide is 3.9 mol %. If this stream were fed directly into the distillation column, these inert components would build up in the condenser and blanket the condenser. Either a high pressure or a low temperature would be needed in the condenser, which may require the use of expensive refrigeration.

Therefore, a flash tank is used to remove most of the light components before feeding into the column. The flash tank is operated at 2 bar. The gas (224.8 kmol/h) is compressed to 110 bar and recycled to the reactor. The compressor power is 1.341 MW.

The liquid from the flash tank is pumped into a 42-stage distillation column on stage 27. The column operates at 1 bar, and a reflux-drum temperature of 50 °C is used so that cooling water can be used in the condenser. A small vapor stream from the top of the reflux drum recycles the small amount of inert components entering the column. This small vapor stream (0.0669 kmol/h) is compressed back up to 110 bar (work is 4.9 kW).

There are three specifications in this column. Two specifications set the compositions of the bottoms (0.01 mol % methanol) and the distillate (0.1 mol % water). The third specification sets the reflux-drum temperature at 50 °C, which establishes the amount of vapor that must be removed from the top of the reflux drum for compression and recycle.

The methanol/water separation is reasonably easy, so the required reflux ratio is only 0.407. The reboiler energy is 54.8 MW. Low-pressure steam (160 °C and 6 bar) can be used in the reboiler since the base temperature is 110 °C.

## 3. Reaction Kinetics

The chemistry of the methanol process involves the reaction of both carbon dioxide and carbon monoxide with hydrogen.

$$CO + 2H_2 \Leftrightarrow CH_3OH CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$$
(1)

The kinetics are given by vanden Bussche and Froment<sup>2</sup> in the following form by using the water-shift reaction:

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$$CO_{2} + 3H_{2} \Leftrightarrow CH_{3}OH + H_{2}O$$

$$CO_{2} + H_{2} \Leftrightarrow CO + H_{2}O$$
(2)

The reactions are exothermic and use a solid catalyst. The kinetics are described by LHHW-type equations (Langmuir–Hinshelwood–Hougen–Watson). Conversion of the reaction rate equations and their units given in the original paper into the form required by Aspen Plus is a daunting task. The original data use pressures in bar and reaction rates in kmol min<sup>-1</sup> kg<sup>-1</sup> catalyst. These must be transformed to use Pascals. This transformation was provided by Emmanuel Lejeune from Aspen Support, and this invaluable assistance is gratefully acknowledged.

The LHHW kinetic structure has the form

$$R = (\text{kinetic term}) \frac{(\text{driving-force term})}{(\text{adsorption term})}$$
(3)

,

The reaction rate for the first reaction for the production of methanol from carbon dioxide is given in eq 4.

$$R_{1} = (k_{4}p_{CO_{2}}p_{H_{2}}) \frac{\left[1 - \frac{1}{K_{E1}} \left(\frac{p_{CH_{3}OH}p_{H_{2}O}}{p_{CO_{2}}p_{H_{2}}^{3}}\right)\right]}{\left[1 + k_{3} \left(\frac{p_{H_{2}O}}{p_{H_{2}}}\right) + k_{1} \sqrt{p_{H_{2}}} + k_{2} p_{H_{2}O}\right]^{3}}$$
(4)

The reaction rate for the water-shift reaction is given in eq 5.

$$R_{2} = (k_{5}p_{CO_{2}}) \frac{\left[1 - \frac{1}{K_{E2}} \left(\frac{p_{CO}p_{H_{2}O}}{p_{CO_{2}}p_{H_{2}}}\right)\right]}{\left[1 + k_{3} \left(\frac{p_{H_{2}O}}{p_{H_{2}}}\right) + k_{1} \sqrt{p_{H_{2}}} + k_{2}p_{H_{2}O}\right]}$$
(5)

Table 1 gives the kinetic and adsorption parameters entered into the Aspen LHHW reaction model to implement these kinetics.

Since the reactions are exothermic, the chemical equilibrium constants decrease with increasing temperature. Therefore, low reactor temperatures should improve conversion, provided they are not so low that the specific reaction rates are too small. For a given reactor size and a desired conversion, the recycle flow rate increases as reactor temperatures are lowered, which means higher compressor work.

The reactor is simulated in Aspen using the RPLUG model with a "constant medium temperature" as the dynamic heattransfer selection. The reactor is cooled by generating saturated steam, and the temperature of the boiling water on the shell side of the reactor tubes is the same at all axial positions. The selection of the medium temperature inferentially sets the reactor temperature profile.

The medium temperature is set at 264 °C so that high-pressure steam (254 °C and 42 bar) can be generated. Thus, one of the important design optimization variables (reactor temperature) is established a priori so that valuable high-pressure steam can be generated, which can be used to drive compressors.

## 4. Overall and per Pass Conversion

With the design conditions and equipment sizes shown in Figure 1, there are 28 920 kmol/h of hydrogen entering the reactor, 4066 kmol/h of carbon monoxide, and 3976 kmol/h of carbon dioxide. The corresponding component flow rates leaving the reactor are 21 673, 1468, and 3292 kmol/h, which means

**Table 1. Kinetic LHHW Parameters** 

$R_1 (\mathrm{CO}_2 + 3\mathrm{H}_2 \rightarrow \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O})$					
kinetic factor $k = 1.07 \times 10^{-3}$					
$E = 36\ 696\ kJ/kmol$					
driving-f	force expressions				
term 1					
conc. exponents for reactants:	$CO_2 = 1; H_2 = 1$				
conc. exponents for products: coefficients: term 2	$CH_3OH = 0; H_2O = 0$ A = -23.02581; B = C = D = 0				
conc. exponents for reactants:	$CO_2 = 0; H_2 = -2$				
conc. exponents for products: coefficients:	$CH_{3}OH = 1; H_{2}O = 1$ A = 24.388981; B = -7059.7258; C = D = 0				
adsorp	tion expression				
adsorption term exponent: concentration exponents:	3				
term 1:	$H_2 = 0; H_2O = 0$				
term 2:	$H_2 = -1; H_2O = 1$				
adsorption constants:					
term 1: term 2:	A = 0, B = 0, C = 0, D = 0 A = 8.1471087, B = 0, C = 0, D = 0				
$R_2 (\mathrm{CO}_2 + \mathrm{H}_2 \rightarrow \mathrm{CO} + \mathrm{H}_2 \mathrm{O})$					
kinetic factor	$k = 1.22 \times 10^9$ E = 94765  kJ/kmol				
driving-1	force expressions				
term 1					
conc. exponents for reactants:	$CO_2 = 1; H_2 = 0$				
conc. exponents for products:	$CO = 0; H_2O = 0$ A = -11512052; B = C = D = 0				
term 2	A = -11.512952, B = C = D = 0				
conc. exponents for reactants:	$CO_2 = 0; H_2 = -1$				
conc. exponents for products:	$CO = 1; H_2O = 1$				
coefficients:	A = -16.184871; B = 4773.2589; C = D = 0				
adsorp	tion expression				
adsorption term exponent: concentration exponents:	1				
term 1:	$H_2 = 0; H_2O = 0$				
term 2:	$H_2 = -1$ ; $H_2O = 1$				

that the per-pass conversion of hydrogen is 25%, the per-pass conversion of carbon monoxide is 64%, and the per-pass conversion of carbon dioxide is 17%.

A = 0, B = 0, C = 0, D = 0

A = 8.1471087, B = 0, C = 0, D = 0

adsorption constants:

term 1:

term 2:

The overall conversion of the carbon monoxide and carbon dioxide in the fresh synthesis gas feed to methanol is 96%. There are 2630 kmol/h of carbon dioxide and 785 kmol/h of carbon monoxide in the synthesis gas, totaling 3415 kmol/h. The methanol in the distillate product is 3278 kmol/h.

Two moles of hydrogen are needed to react with the carbon monoxide, and three moles of hydrogen are needed to react with the carbon dioxide. If there were complete conversion of all the carbon dioxide and carbon monoxide in the synthesis gas feed, the hydrogen consumed in the reactions would be 2630  $\times$  2 + 786  $\times$  = 7616 kmol/h of hydrogen. The hydrogen supplied in the fresh synthesis gas feed is 7724 kmol/h. So there is a small excess. The overall conversion of hydrogen to produce methanol is quite high (98.6%).

These high conversions of reactants indicate that the design has achieved only small losses of the valuable reactants, despite the need to purge out the inert components in the fresh feed (methane and nitrogen). The economics discussed in a later section demonstrate that energy and capital can be expended to improve yield so that losses of reactants and products are very



Figure 2. Txy diagram for methanol/water at 1 bar.

small. Douglas<sup>3</sup> established this principle in his pioneering work on conceptual process design over two decades ago.

It should be noted that an alternative design could be developed if medium- or low-pressure steam were generated in the reactor. Low-pressure steam (160 °C and 6 bar) could be generated if the medium temperature were set at 170-180 °C, and this steam could be used in the reboiler of the distillation column. The resulting lower reactor temperatures would result in a smaller reactor and less recycle. This alternative design is not considered in this paper.

#### 5. Phase Equilibrium

There are two vapor—liquid flash separations in the process. The Aspen "Flash2" model is used in the separator block and the flash block. Most of the light components are removed in the vapor streams leaving these vessels, but small amounts of light components are dissolved in the liquid streams. This is what necessitates the need for the flash tank and the vapor stream from the reflux drum.

The methanol/water separation is nonideal but fairly easy. The van Laar equations are used in the distillation column. Figure 2 gives a Txy diagram at 1 bar pressure.

## 6. Effects of Design Optimization Variables

The methanol process has a number of design optimization variables that impact energy and capital economics in conflicting ways. We explore these effects quantitatively in this section.

**6.1. Economic Basis.** The economics consider both capital investment (compressors, heat exchangers, reactor, catalyst, separator tank, flash tank, and column) and energy costs (compressor work, steam used in the reactor preheater, and reboiler duty in the column). Table 2 summarized the sizing and cost basis used in this analysis. These parameters are taken from Douglas<sup>3</sup> and Turton et al.<sup>4</sup>

The compressors use electricity at \$16.8 per GJ. The reactor preheater uses medium-pressure steam at \$8.22 per GJ. The column reboiler uses low-pressure steam at \$7.78 per GJ.

There are two credits in the economics. One is for the steam generated in the reactor. It is at high-pressure but is saturated, not superheated, so \$6 per GJ is assumed for its value. The second is the heating value of the vent stream, which contains mostly hydrogen and methane with some carbon monoxide. These components can be burned to recover heat. The amount of air to completely combust each component, the component heats of combustion, and the mean heat capacities of the resulting nitrogen, carbon dioxide, and water gas stream are

<b>Fable</b>	2.	Basis	of	Economics	and	Equipment	Sizing	
		200000	~	neomonies	*****	nderburgene		

column diameter: Aspen tra	ay sizing
column length: NT trays w	ith 2 ft spacing plus 20% extra length
column vessel (diameter an	d length in meters)
	capital cost = 17 640 (D) <sup><math>1.066</math></sup> (L) <sup><math>0.802</math></sup>
condensers (area in m <sup>2</sup> )	
	heat-transfer coefficient = $0.852 \text{ kW/K} \cdot \text{m}^2$ differential temperature = reflux-drum temperature -303 K capital cost = 7296(area) <sup>0.65</sup>
reboiler (area in m <sup>2</sup> ):	
	heat-transfer coefficient = $0.568 \text{ kW/K} \cdot \text{m}^2$ differential temperature = 34.8 K capital cost = 7296(area) <sup>0.65</sup>
reactor and feed-effluent he	eat exchanger (area in m <sup>2</sup> ):
	capital cost = 7296(area) <sup>0.65</sup> heat-transfer coefficient FEHE = 144 kcal h <sup>-1</sup> K <sup>-1</sup> m <sup>-2</sup> heat-transfer coefficient reactor = 244 kcal h <sup>-1</sup> K <sup>-1</sup> m <sup>-2</sup>
catalyst cost - \$10/kg	
compressor capital cost = (	(1293)(517.3)(3.11)(hp) <sup>0.82</sup> /280
energy cost	
	LP steam = \$7.78 per GJ MP steam = \$8.22 per GJ HP seturated steam from reactor =

MP steam = \$8.22 per GJ HP saturated steam from reactor \$6.00 per GJ electricity = \$16.8 per GJ

TAC = capital cost/payback period + energy cost

payback period =3 years

used to find the heating value of the vent stream (0.331 kJ/kmol). The sensible heat of changing the combustion products from ambient up to a 260 °C stack gas temperature is subtracted from the heat of combustion. A value of \$6 per GJ is used for this fuel.

The assessment of economics uses the income derived from the process for a fixed amount of synthesis gas fed. The value of methanol is assumed to be \$2 per gallon (\$21 per kmol). In all cases, the fresh feed of synthesis gas is fixed at 11 450 kmol/ h. As design parameters change, the amount of product methanol changes, the amount of venting changes, the amount of reactor steam changes, and the energy consumption changes (compressors, reactor preheater, and column reboiler).

We define income as the sum of the value of the methanol produced plus the value of the vent and reactor steam credits minus the energy costs minus the annual capital cost.

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income = (flow rate methanol)($value) + (flow rate vent)($value)
+ (reactor steam)($value) - (work of 5 compressors)($/MW)
- (reboiler energy)($/MW) - \left(\frac{\text{total capital}}{3}\right) (6)
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Total capital investment includes the cost of the five compressors, the intercooler between the feed compressors, the feed-effluent heat exchanger, the reactor preheater, the reactor with catalyst, the cooler/condenser, the separator vessel, the flash drum, the distillation column vessel, the condenser, and the reboiler.

We choose to look at income instead of profit because this avoids having to assign a value for the synthesis gas feed. The incremental increase in income when changing a design parameter and the incremental increase in the required capital



Figure 3. Effect of reactor pressure.

investment are evaluated to see if the incremental return on investment is sufficient to justify the investment.

As the numbers given in the following sections will reveal, the value of the product is an order of magnitude larger that the cost of energy and capital. Douglas<sup>3</sup> pointed out this basic design principle many years ago. Small increases in product yield are worth more than the corresponding required increases in capital and energy to achieve them. This is true up to a point.

In the following sections, the effects of variables on the economics of the process are studied one at a time to present a clear picture of the trends. After each variable is explored, the dominant variables are varied in an iterative procedure to arrive at the optimum values of the design variables.

**6.2. Effect of Pressure.** High pressure in the reactor favors the production of methanol because of the increase in reactant partial pressures. Both reactions are nonequimolar with fewer molecules of products than reactants. So Le Chatelier's principle would indicate that high pressure drives the reactions to the right. The higher the pressure, the smaller the reactor can be with a given recycle flow rate, which reduces reactor vessel and catalyst capital investment. With a given size of the reactor, the higher the pressure, the smaller the recycle flow rate can be, which reduces recycle compression energy and recycle compressor capital investment.

However, the higher the pressure, the more compression of the feed synthesis gas is required. The synthesis gas is assumed to be supplied at 51.2 bar from an upstream unit. A two-stage compressor system is used with intermediate cooling. Following the common design heuristic, the compression ratio is specified to be the same in both stages. For a given synthesis gas pressure  $P_1$  and a system pressure  $P_2$ , the compression ratio in each stage of a two-stage compression system is  $\sqrt{(P_2/P_1)}$ .

Figure 3 and Table 3 show the effects of changing pressure on a number of important variables. These results are generated with the other design optimization variable set at reasonable initially guessed values. The number of reactor tubes is 5000, the flash tank pressure is 10 bar, and the vent/recycle split fraction is 0.025. This split affects the composition of the inert components in the recycle gas. The number of stages in the distillation column is set at 42 with feed on stage 20. All of these variables will be optimized later.



Table 3. Effect of Pressure<sup>a</sup>

system pressure (bar)	90	100	110	120	130
compressor K1 (MW)	3.254	3.901	4.499	5.053	5.571
compressor K2 (MW)	3.254	3.899	4.483	5.037	5.559
compressor K3 (MW)	1.303	1.109	0.958	0.841	0.747
D1 (kmol/h)	3254.7	3272.7	3287.3	3299.5	3309.7
vent (kmol/h)	1069.0	1008.8	957.9	915.9	879.0
recycle (kmol/h)	41 690	39 343	37 358	35 720	34 281
QHX1 (MW)	4.444	5.101	5.709	6.272	6.798
total capital (\$10 <sup>6</sup> )	32.55	34.74	36.70	38.53	40.21
total energy (\$ 10 <sup>6</sup> per yr)	18.83	19.41	19.92	20.42	20.86
income (\$ 10 <sup>6</sup> per yr)	482.48	483.34	483.96	484.33	484.57
incremental capital (\$)		2 192 000	1 961 100	1 830 000	1 679 000
incremental income (\$ per yr)		860 000	618 000	373 000	239 000
incremental ROI (%)		39.2	31.5	20.4	14.2

<sup>a</sup> 5000 tubes, 10 bar flash, 0.025 split.

The top left graph in Figure 3 shows that compressor work in the feed compressors increases when the system pressure is increased. The work in the first compressor K1 is shown, and the work in the second compressor K2 is essentially the same as that in K1. The changes in compressor work are quite significant and impact both energy cost (expensive electrical energy at \$16.8 per GJ) and compressor capital investment (see Table 2).

On the other hand, the top right graph in Figure 3 shows that the required recycle flow rate decreases as the pressure increases. This reduces the cost of compression of the gas recycle in compressor K3 (second graph from the top on the left in Figure 3). The net effect is an increase in total capital cost and total energy cost (third graphs from the top in Figure 3).

The bottom two graphs show that the production rate (D1) of the methanol product gradually increases as the pressure is increased, which produces a gradual rise in income despite the increases in both energy cost and capital cost. Remember that the feed of synthesis gas is fixed. The increase in product is accompanied by a corresponding decrease in the vent rate (second graph on the right in Figure 3). There are smaller losses of reactants in the vent stream as pressure increases because of the improvement in kinetics.

However, capital investment increases as pressure rises, so we need to see if the incremental investment is justified by the



Figure 4. Effect of reactor size.

Table 4. Effect of Reactor Size<sup>a</sup>

tube number	5000	6000	7000	8000	9000	10000
recycle (kmol/h)	37351	36869	36507	36247	36044	35897
D1 (kmol/h)	3287.34	3291.09	3293.93	3295.96	3297.52	3298.66
compressor K3 (MW)	0.9580	0.9453	0.9356	0.9289	0.9231	0.9197
vent (kmol/h)	957.7	945.4	936.1	929.4	924.2	920.4
RX+k3 Capital (\$10 <sup>6</sup> )	6.238	6.7592	7.2705	7.7751	8.2705	8.7618
income (\$10 <sup>6</sup> per yr)	491.83	492.23	493.49	492.63	492.70	492.71
incremental capital (\$)		521 200	511 300	504 600	495 400	491 300
incremental income (\$ per yr)		400 000	260 000	140 000	70 000	10 000
incremental ROI (%)		77	51	28	14	2

<sup>a</sup> 110 bar, 10 bar flash, 0.025 split.

incremental increase in income. The detailed numbers are presented in Table 3. Moving from 90 to 100 bar provides an \$860 000 increase in income and requires a \$2 192 200 increase in capital investment. The incremental return on investment is a healthy 39%.

Evaluating the move from 100 to 110 bar shows a 31% incremental return on incremental investment. Going from 110 to 120 bar yields a 20% return, and going from 120 to 130 bar yields a 14% return. These results clearly demonstrate that there is a point of diminishing returns for investing capital. A system pressure of 110 bar is selected as the design value.

**6.3. Effect of Reactor Size.** Using a pressure of 110 bar and holding the other design optimization variables constant, the effect of changing the number of tubes in the reactor is explored. Tube diameter is kept constant at the smallest practical value (0.03675 m) to provide the maximum heat-transfer area per unit volume. Tube length is kept constant to provide a reasonable pressure drop through the reactor (1.5 bar).

Increasing the reactor size will increase the capital investment in both the multitube vessel and the catalyst inside the tubes. However, the per-pass conversion should increase, so the required recycle flow rate would decrease. This will decrease compressor work in the recycle compressor K3 and also decrease its capital cost.

Figure 4 shows the effect of changing the number of reactor tubes on several important variables. The upper left graph shows that capital investment in the reactor vessel, catalyst, and K3 compressor increases as more tubes are used. All the other units

are essentially unaffected by changes in reactor size. The middle left graph shows that there is a decrease in recycle, which results in a decrease in work in the recycle compressor K3 (top right graph) and its capital cost. The effect of increases in reactor vessel and catalyst capital is larger than the effect of decreases in compressor capital, so the total capital investment in these two units increases.

The larger reactor improves the yield of methanol, as reflected in the gradual increase in the distillate D1, which is the methanol product stream (bottom left graph in Figure 4). The vent flow rate decreases as the product flow rate increases (middle right graph in Figure 4) because the flow rate of synthesis gas is fixed.

Income increases gradually, but the rate of increase slows down as more tubes are added. Table 4 gives details of the economics. Return on investment calculations show a gradual decrease in the incremental return on incremental investment. Going from 7000 to 8000 tubes gives a 28% return. Going from 8000 to 9000 gives a small 14% return on investment.

A reactor with 8000 tubes in selected.

**6.4. Effect of Vent/Recycle Split.** All of the previous designs have used a vent-to-recycle split of 0.025. The resulting inert component compositions in the vent stream are about 26 mol % methane and 3 mol % nitrogen. The remaining components represent losses of reactants hydrogen, carbon monoxide, and carbon dioxide. Lowering the split ratio (vent less) will increase the composition of the inert components in the vent and reduce reactant losses in the vent, which only has fuel value.



Figure 5. Effect of vent/recycle split.

On the other hand, having lower concentrations in the recycle gas going to the reactor will adversely affect kinetics and require higher recycle flow rates, which will increase recycle compressor costs. So there is a trade-off between vent losses and recycle compressor energy and capital costs.

In order to accurately show the effects of higher recycle gas flow rates around the gas loop, pressure drops through the various units in the loop are varied with recycle flow rate. The base-case pressure drop around the loop is 3 bar: 0.5 bar through both sides of the FEHE, 1.5 bar through the reactor, 0.1 bar through the reactor preheater, and 0.4 bar through the condenser. The base-case recycle flow rate is 36 200 kmol/h. Pressure drops change with the square of the flow rate changes. The discharge pressure of the feed compressors is kept at 110 bar.

Figure 5 shows that recycle flow rates increase as the split ratio is *decreased* (second graph from the top on the left), as does the work of the recycle compressor K3 (top right graph). Vent rates decrease, and methanol product rates increase as the split ratio is decreased. But both capital investment and energy costs increase when the split ratio is decreased. A split ratio of 0.022 gives the maximum income.

Moving from a split ratio of 0.023 down to 0.022 gives an incremental increase in income of \$620 000 per year and requires only a \$25 000 increase in capital investment. Moving from 0.022 down to 0.021 produces a *decrease* in income while at the same time increasing capital investment. Therefore, a split ratio of 0.022 is selected.

**6.5. Effect of Reactor Flash Pressure.** A flash-tank pressure of 10 bar has been used in all the previous designs. This design optimization variable is now explored with all the other variables fixed: 110 bar pressure, 8000 tubes, and a split ratio of 0.022.

The flash tank's job is to keep inert components out of the distillation column. The lower the flash pressure, the fewer inert components enter the column, which reduces the vapor coming off the top of the reflux drum, thus reducing costs of the compressor K4 on this stream. On the other hand, lowering flash pressure results in more vapor leaving the flash tank, which increases the energy and capital cost of the compressor (Kflash) that is recycling this stream back to the 110 bar reactor pressure. So there is a trade-off between the cost of the two compressors, which are affected in opposite ways by flash pressure.



Figure 6 illustrates all of these trends. The top two graphs show that the vapor V1 from the reflux drum of the distillation column decreases as the flash pressure is decreased. This reduces the work in compressor K4. Once the flash pressure gets down to 2 bar, there are only very small amounts of inert components entering the column.

However, the flow rate of vapor leaving the flash tank increases as flash pressure is decreased, as shown by the increase in compressor work (middle left graph in Figure 6). Going from 2 to 1 bar results in a rapid change in Kflash compressor work. A pressure of 2 bar gives the maximum income and at the same time gives the minimum capital investment. So the flash drum pressure is set at 2 bar.

It is interesting to note that there is an additional advantage of running a low flash-drum pressure. The reduction in the amount of inert components coming into the reflux drum of the column improves the purity of the methanol product. The specification used is 0.1 mol % water in the distillate, but there is some carbon dioxide present in the liquid product. With a flash-drum pressure of 2 bar, the carbon dioxide composition is 0.9 mol % in the distillate, which gives a methanol purity of 98.9 mol %. With a flash-drum pressure of 1.5 bar, the carbon dioxide composition is 0.7 mol % in the distillate, which gives a methanol purity of 99.2 mol %. With a flash-drum pressure of 1 bar, the carbon dioxide composition is 0.5 mol % in the distillate, which gives a methanol purity of 99.4 mol %. So if very high purity methanol is desired, a low flash-drum pressure would be required.

**6.6. Optimum Distillation Column Design.** The last design optimization variable explored is the number of stages and the feed-stage location in the distillation column. The values that minimize total annual cost were determined. The results are shown in Table 5. The optimum feed stage is found for each case by determining the feed stage that minimizes reboiler heat input.

As the number of total stages is increased, energy costs and heat exchanger capital costs decrease, but the capital cost of the shell increases. Total capital increases with increasing stages. The 42-stage column has the lowest total annual cost.

Note that the variation of the economic objective function (TAC) with total stages is quite modest, with less than 1%



Figure 6. Effect of flash tank pressure.

Table 5. Optimum Distillation Column Design

NT	32	42	52
NFopt	19	27	30
ID (m)	5.979	5.806	5.674
QR (MW)	59.85	54.27	54.26
QC (MW)	48.45	47.83	47.79
area reboiler (m <sup>2</sup> )	2770	2741	2740
area condenser (m <sup>2</sup> )	2838	2802	2800
capital costs $(10^6 \)$			
shell	1.318	1.623	1.928
reboiler and condenser	2.542	2.523	2.522
energy cost (\$10 <sup>6</sup> /yr)	13.46	13.32	13.31
TAC (\$10 <sup>6</sup> /yr)	14.75	14.70	14.80

change over the entire range from 32 to 52 stages. Thus, a rigorous determination of precisely the optimum number of stages, narrowing it down to a precision of a single stage, is unnecessary.

Figure 7 gives the temperature and composition profiles in the distillation column. These will be used in developing a control structure later in this paper.

The flowsheet shown in Figure 1 shows the final design. The system pressure is 110 bar, the reactor has 8000 tubes, the vent/ recycle split is 0.022, the flash-drum pressure is 2 bar, and the column has 42 stages. An effective plantwide control scheme for the process is developed and tested in the next section.

# 7. Plantwide Control

Before exporting the steady-state Aspen Plus simulation into Aspen Dynamics, the size of the reflux drum and column base in the distillation column are sized to provide 5 min of liquid holdup when at the 50% level. The size of the reactor and column vessel are known from the steady-state design. The sizes of the separator and flash drum were also determined during steady-state design so that their capital investment costs could be calculated. The size of the separator is set by the maximum superficial vapor velocity, using the gas flow rate and its density. An F-factor of 0.5 is used (in English engineering units). The diameter is 6.5 m since there is a very large gas recycle stream.



Figure 7. (A) Column temperature profile. (B) Column composition profiles.

The size of the flash tank is set by 5 min of liquid holdup (2.8 m diameter, 5.6 m length). The compressors and heat exchangers are assumed to have negligible dynamic lags.



Figure 8. Plantwide control structure.

The development of the plantwide control structure presented below is based on the heuristic procedure proposed a decade ago<sup>5</sup> that has been successfully applied to many industrial processes.

**7.1. Control Structure.** Figure 8 shows the plantwide control structure developed for this process. Conventional PI controllers are used in all loops. All level loops are proportional with  $K_C = 2$ . Flow controllers that manipulate compressors use a gain of 0.5 and an integral time of 0.5 min. The column tray temperature controller has a 1 min deadtime. The reactor temperature loop has a 2 min deadtime to account for the steam generation dynamics. The composition controller has a 3 min deadtime. These temperature and composition controllers are tuned by using relay-feedback tests to obtain ultimate gains and periods and then applying Tyreus–Luyben tuning rules.

All of the loops are listed below with their controlled and manipulated variables.

1. The synthesis gas is flow controlled by manipulating work to compressor K1. If the synthesis gas is being generated in an upstream gasification unit, a pressure controller in that unit typically would change the set point of the flow controller.

2. The temperature of the compressed gas leaving the interstage cooler is controlled by manipulating heat removal in the heat exchanger (cooling water).

3. The suction pressure of the second compressor K2 is controlled by manipulating its compressor work.

4. The reactor inlet temperature is controlled by manipulating the heat input to the reactor preheater (medium-pressure steam).

5. The temperature of the gas leaving the condenser and going into the separator is controlled by manipulating the heat removal (cooling water) in the condenser.

6. A composition controller manipulates the control valve in the vent stream to maintain the composition of methane in the gas recycle.

7. A high-pressure override controller can also change the position of the control valve in the vent line if the separator pressure exceeds some specified value. A high-selector chooses which signal positions the vent valve. The setup and the need for this controller are discussed below.

8. The liquid level in the separator is controlled by manipulating the liquid flow rate from the separator into the flash tank.

9. The pressure in the flash tank is controlled by manipulating work in the Kflash compressor, which recycles the gas back to the reactor.

10. The liquid level in the flash tank is controlled by manipulating the liquid flow rate from the flash tank into the distillation column.

11. Base liquid level in the column is controlled by manipulating bottoms flow rate. This is the water product stream leaving the process.

12. Reflux-drum level is controlled by manipulating distillate flow rate. This is the methanol product stream leaving the process.

13. The reflux is ratioed to the feed to the column using a multiplier that adjusts the set point of a flow controller on the reflux. The feed flow rate is the other input to the multiplier.

14. Column pressure is controlled by manipulating condenser heat removal (cooling water).

15. The temperature on stage 35 is controlled by manipulating reboiler heat input (low-pressure steam).

16. The small vapor stream from the top of the reflux drum is flow controlled by manipulating work in compressor K4.

Note that the throughput is set by the synthesis gas flow rate into the process, and inventory loops are in the direction of flow. Note also that the pressure in the system is *not* controlled but floats up and down as throughput and synthesis gas composition change. Further discussions and the rationale for the important loops are given below.

**7.2. Column Control Structure Selection.** Many industrial distillation columns use some type of single-end temperature control because of its simplicity and low maintenance cost. However, this simple structure may not provide effective control for some columns. Even if a single-end control structure is possible, we have to decide how to select the other control degree of freedom. The most common choices are holding a constant reflux-to-feed ratio or holding a constant reflux ratio.

A. Selecting Reflux Ratio or Reflux-to-Feed Ratio. To explore this question, a series of steady-state runs are made in

Table 6. Column Control Structure Selection

	feed composition	reflux-to-feed ratio	reflux ratio
Design	0.86517 MeOH	0.3355	0.3771
	0.81517 MeOH	0.3297	0.4071
	0.76517  MeOH $0.22674 \text{ H}_2\text{O}$	0.3394	0.385

which the effects of changes in feed composition on the required changes in reflux-to-feed ratio and reflux ratio are determined while holding both products at their specified compositions. Table 6 gives results of these calculations.

The required changes in the reflux-to-feed ratio (R/F) are only about 3% over the entire range of feed compositions from 86.5 to 76.5 mol % methanol. An appropriate change in the water feed composition is made as the methanol composition is varied. The required changes in the reflux ratio (RR) are much larger (about 16%). Therefore, from a steady-state standpoint, the R/F control structure should handle feed composition disturbances better than the RR control structure.

**B.** Selecting Temperature/Composition Control Tray Location. Another important issue in distillation control is the location of the tray whose temperature is to be controlled in a single-end structure. There are many methods for making this selection, but a simple and effective approach is to select a tray where there are significant changes in temperature from tray to tray.

Figure 7A shows a large change in the temperature profile in the lower part of the column. Stage 35 is selected, which has a temperature of 101 °C. The controller parameters that result from relay-feedback testing are given in Table 7.

**7.3. High-Pressure Override Controller.** As the dynamic simulation results presented in the next section will demonstrate, there is no need for an override controller when disturbances in throughput occur. The design values of the composition of the synthesis gas provide the necessary balance between the carbon monoxide and carbon dioxide fed and the hydrogen fed so as to satisfy the stoichiometry of the two reactions. Two moles of hydrogen are required for each mole of carbon monoxide. Three moles of hydrogen are required for each mole of carbon dioxide.

There are 2630 kmol/h of carbon monoxide in the synthesis gas that require 5260 kmol/h of hydrogen. There are 785.3 kmol/h of carbon dioxide in the synthesis gas that require 2356 kmol/h of hydrogen. Thus, the total hydrogen required to completely react all the carbon monoxide and carbon dioxide is 7616 kmol/h. The hydrogen in the synthesis gas feed is 7839 kmol/h, so there is a slight excess, which leaves the system in the vent stream along with the unreacted carbon monoxide and carbon dioxide.

If the synthesis gas composition changes such that this delicate stoichiometric balance no longer holds, the compo-

nent(s) in excess will build and pressure will increase in the system. Remember that the feed into the system is flow controlled. Therefore, a strategy to handle this problem is required.

An override controller is a simple way to achieve this objective. The vent valve is air-to-open (fails shut). A high selector chooses between the higher of two signals. The first signal comes from the composition controller. This signal normally sets the vent valve position. The second signal comes from the high-pressure override controller whose output signal only increases and takes over the vent valve when the separator pressure get above 120 bar. The override controller is proportional-only with a gain of 5 and a normal output signal of 0%. As pressure changes from 120 to 140 bar, its output signal changes from 0 to 100%. At some pressure, this output will exceed the signal coming from the composition controller and begin opening the vent valve.

The synthesis gas composition disturbances discussed below demonstrate the effectiveness of the proposed control structure.

**7.4. Dynamic Performance Results.** Several large disturbances are made to test the ability of the proposed plantwide control structure. These disturbances include synthesis gas feed flow rate and synthesis gas composition (adding more inert methane or changing the relative amounts of the reactants).

**A. Throughput Disturbances.** Figure 9 gives results for 20% changes in the set point of the synthesis gas flow controller. The solid lines are 20% increases; the dashed lines are 20% decreases. The disturbances are made at 0.2 h.

Stable regulatory control is achieved. Notice that the pressure in the separator (bottom left graph in Figure 9A) rises up to a new steady-state level for increases in throughput and drops to a lower level for decreases in throughput. The pressure in the gas loop (FEHE, preheater, reactor, and separator) is *not* controlled in this plantwide control structure but varies with conditions in the reactor that affect reaction rates.

Recycle, distillate, and bottoms flow rates increase as throughput increases. The coolant temperature (Tcool) in the reactor decreases as throughput increases so that the increased heat removal can be achieved by providing a larger differential temperature driving force (second from the bottom right graph in Figure 9A).

Stage 35 temperature is well controlled by manipulating reboiler heat input (third graphs from the top in Figure 9B). The R/F ratio system changes the column reflux R1 as the feed to the column F1 changes (bottom graphs in Figure 9B).

Of primary importance, the compositions of the two products leaving the process are held quite close to their specified values. The distillate composition  $x_{D(M)}$  and the bottoms water composition  $x_{B(W)}$  remain near their specifications (top and second graphs on the right in Figure 9B).

**B.** Methane Impurity in Synthesis Gas Feed. Figure 10 gives results for changes in the methane impurity in the synthesis

**Table 7. Controller Parameters** 

	TCRX	TC1	CCvent	high PC
controlled variable manipulated variable	reactor exit temperature steam temperature	stage 35 temperature reboiler heat input	recycle gas composition signal to high selector on vent valve position	separator pressure signal to high selector on vent valve position
SP	267 °C	101 °C	0.258 mf CH <sub>4</sub>	130 bar
transmitter range	200 – 300 °C	50 – 150 °C	0-0.5 mf CH <sub>4</sub>	120-140 bar
OP	264 °C	45.38 Gcal/h	14.77%	0%
OP range	200 – 300 °C	0 - 90.77 Gcal/h	0-100%	0-100%
deadtime	2 min	1 min	3 min	
K <sub>C</sub>	0.456	1.37	5.0	5
$ au_{ m I}$	9.2 min	9.2 min	56 min	



Figure 9. (A and B) 20% feed flow rate disturbances.

gas. The design value of this inert impurity is 2.17 mol % methane. The design hydrogen feed composition is 67.46 mol % hydrogen. The solid lines show results for an increase in methane impurity to 3.17 mol % and an appropriate decrease in hydrogen composition to 66.46 mol %. The dashed lines show results for a decrease in methane impurity to 1.17 mol % and an appropriate increase in hydrogen composition to 68.46 mol %.

First, let us consider the effects of increasing the methane impurity in the synthesis gas. There is a substantial increase in the vent flow rate (second left graph from the top in Figure 10A), which results in higher losses of the reactants. Consequently, less methanol D1 and water B1 are produced (first and second left graphs in Figure 10B). The pressure in the system goes down (Psep in bottom left graph in Figure 10A). Product purities are held close to their specifications.

Now consider the effects of decreasing the methane impurity in the synthesis gas. More products are made because the vent flow rate decreases, meaning smaller losses of reactants. Product purities are again held close to their specifications.

However, this disturbance shows the need for the highpressure override controller. Notice that the recycle gas methane composition is *not* held at its set point (second right graph in Figure 10A) but drifts downward. This occurs because the pressure in the gas loop Psep (bottom left graph in Figure 10A) starts to increase. When the pressure gets up to 120 bar, the override controller takes over control of the vent valve and opens it to maintain system pressure.



Figure 10. (A and B) Feed methane composition disturbances.

**C. Reactant Concentrations in Synthesis Gas Feed.** Figure 11 also demonstrates the need for the override controller. The disturbances are changes in the carbon monoxide, carbon dioxide, and hydrogen compositions in the feed.

(1) CO/CO2 Ratio: The solid lines give results for the case in which the feed contains more carbon dioxide and less carbon monoxide. Carbon dioxide is changed from 6.858 to 8.858 mol %. Carbon monoxide is changed from 22.97 to 20.97 mol %.

As expected, more water is produced (B1 increases) since there is more carbon dioxide. The amount of methanol produced (D1) decreases slightly because the vent rate increases from 872 to 939 kmol/h, so reactant losses increase. There is a slight drop in methanol purity.

Pressure increases from 110 to 115.9 bar, so the override controller does not come into action for this disturbance. The vent methane composition controller is able to maintain the desired 28.5 mol % methane.

Since carbon monoxide consumes more hydrogen than carbon monoxide, the amount of hydrogen lost in the vent drops from 479 to 207 kmol/h for this disturbance. On the other hand, the amount of carbon dioxide lost increases from 69.8 to 206.9 kmol/h.

(2) Hydrogen to Carbon Ratio: The dashed lines in Figure 11 give results when the synthesis gas composition is changed from 67.46 to 61.46 mol % hydrogen, 22.97 to 25.97 mol % carbon monoxide, and 6.86 to 9.86 mol % carbon dioxide. This disturbance increases the demand for hydrogen by feeding in more carbon monoxide and carbon dioxide but provides less hydrogen.

The result is an initial drop in pressure (bottom left graph in Figure 11A) as the hydrogen is consumed at a higher rate. However, it does not take long for the pressure to start increasing because the carbon monoxide and carbon dioxide are not being consumed due to the shortage of hydrogen. When the pressure builds up to 120 bar, the override controller takes over the vent valve and removes gas from the system. The vent methane composition is not controlled and drops from 28.5 to 15.4 mol % methane.



Figure 11. (A and B) Feed composition disturbances.

The reactor pressure eventually levels out at 131 bar with a very large vent rate (1623 kmol/h). Large losses of reactants in the vent stream occur, so the production of methanol drops from 3311 to 3178 kmol/h. The water produced drops from 707 to 411 kmol/h. The loss of carbon dioxide in the vent climbs from 69.8 kmol/h to a whopping 673 kmol/h. The high reactor pressure requires a huge increase in the work of the Kflash compressor from 1.015 to 8.77 MW.

These results demonstrate the need to provide precise control of the synthesis gas feed by varying conditions in upstream units. For example, if the synthesis gas is being generated from coal in a gasifier, there will be a shortage of hydrogen since coal has a hydrogen-to-carbon ratio of only about one. The synthesis gas is typically split into two streams. One is sent directly to the methanol plant. The other stream is sent to a water-gas shift reactor unit to produce more hydrogen and carbon dioxide from water and carbon monoxide. Then, the carbon dioxide is removed from the gas, typically using amine scrubbing, and the resulting hydrogen-rich stream is combined with the other synthesis gas stream, and the total is fed to the methanol process. The fraction of the synthesis gas fed to the water-gas shift unit must be precisely set so that the methanol plant feed has the correct amount of hydrogen for reaction with the carbon dioxide and carbon monoxide it contains. A discussion of the control structure to achieve this objective will be the subject of a future paper.

## 8. Conclusion

The methanol process presents some interesting design and control features. Design trade-offs exist between reactor pressure and feed compressor energy, between reactor size and recycle flow rate, between venting rate and reactant losses, and between flash pressure and flash compression energy.

The plantwide control structure has the unusual feature of permitting the pressure in the reactor to vary as conditions change. A high-pressure override controller is needed to handle imbalances in the stoichiometry of the reactants in the synthesis gas feed.

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