Methanol Reactor Optimization: Alternate Fuel Source

Elton Amirkhas

Writer's Comment: For a chemical engineering student, the design and optimization of reactors is very important, especially in the petrochemical industry. To get an idea of this concept, I chose to write about methanol reactor optimization. My senior design project was very similar to this topic and I used that as a basis for my writing. I also used previous chemical engineering knowledge and coursework on reactor design and kinetics to connect key ideas throughout the report. My approach to writing this technical report was to first brainstorm major concepts and ideas relating to reactor optimization and put them into writing. Then I began to format the appropriate sections and schematic diagrams that belonged in the report. The revising process, which was difficult and required much planning and insight, focused on the concept of SCC: simplify, clarify, and correct. At the end of the report, I compared what I had written to my senior design project and made sure that everything was coherent and reasonable. This made my report detailed, but also easier to read.

—Elton Amirkhas

Instructor's Comment: Elton Amirkhas' technical report illustrates the excellent value of combining industry internship experience with a University Writing Program writing-in-the-professions course. Elton wrote this paper to fulfill the technical report assignment in my UWP 102E (Writing for Engineers) class. For this paper, I set the standards for rhetorical strategy, document format, and sentence-level style. But I allow my engineering writing students to select an industrial situation that involves a real-world product or process improvement. Students who have not worked in industry have to "fill in the blanks" using library research, networking, and, alas, speculation, but Elton, who has worked as an engineering intern, was able to enrich his paper with application-specific technical details. This technical report showcases many of the problem solving dilemmas that professional chemical engineers face. Elton's topnotch write-up of his process improvement project for Chevron Corporation required him not only to document the project objective and solution criteria given to him by his boss, Mr. Karpay, but also to complete the problem statement by stating a set of complementary assumptions based on his own critical thinking. Thus, this report shines with professionalism, advanced analysis, fine writing, as well as academic savvy.

—Brad Henderson, University Writing Program

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I. Summary

The Chevron Corporation Research and Development Center has discovered that methanol can be used as an alternate fuel source. The marketability of and demand for methanol has been on the rise for the past decade. As a result, Chevron wants to work against its competitors to produce purer methanol and to sell it for profit. The Plant Design Division has decided to purchase and install a new stoichiometric methanol reactor to improve methanol production. A request was made to optimize the reactor at the methanol plant in Richmond, California.

Mr. Karpay, the senior process design engineer at the plant, asked my group to optimize the reactor. The reactor was using natural gas as a key reactant. The methanol production target was 500 mol/hr. Chevron Corp. added economic cost constraints for the reactor. The several key parameters investigated were as follows: reactor volume, reaction rate, reactor temperature, conversion, and methanol output.

We used PID (proportional-integral-derivative) and Cascade controllers to monitor and collect data for the reactor under nominal operating conditions. Moreover, we noted that catalyst suppliers reported that the catalyst being used degrades at 610K. Simulation software was used to simulate operating conditions and to calculate economic cost.

We concluded that the most viable alternative for optimizing the reactor was to increase reactor temperature to just below that of the catalyst degradation temperature. As a result, the economic cost was $24.9M/yr with a conversion of 79%. The corresponding required reactor volume was 171.3 L with a methanol output of 500 mol/hr. That of natural gas was 888 mol/hr.

II. Introduction

Chevron Corporation has been researching and developing alternate fuel sources for the past two decades. Chevron believes that methanol can be used as an alternate fuel source and possibly be used in many chemical applications such as fuel cells. In 2003, Chevron designed a new methanol production plant near Richmond, California, producing roughly 350 mol/hr of methanol.

Just recently, a new stoichiometric methanol reactor was installed at the plant to increase the production of methanol. This reactor was installed to improve methanol output and to increase methanol production from 350 mol/hr to 500 mol/hr across a 330-day/yr operational period. The methanol reactor was using two main reactions, the Fischer-Tropsch reaction and the Water Shift reaction, to produce methanol.

The capital cost of this reactor was estimated to be 20 million dollars, with maintenance costs ranging from $400,000 to $600,000 per year. The cost of the reactor was based on sizing parameters, feed quantities, reaction temperatures, and available kinetic data from suppliers.

Chevron has been worried about its competitors such as Exxon Mobil, Valero, and Shell using and improving upon methanol production. Thus, Chevron created an optimization program in its plant design sector to optimize the currently installed methanol reactor. All downstream processes were operating at nominal levels except the methanol reactor. Next, the methanol reactor needed to be optimized in order to compete against Chevron's competitors.

Mr. Karpay, the senior design engineer in the plant design sector, suggested that the methanol reactor be modified to accommodate higher methanol production rates and to accomplish higher conversions, preferably over 65%. Mr. Karpay explicitly stated that capital costs should be considered along with any related costs in optimizing the reactor. Heat management costs and utilities costs should also be considered. Catalyst suppliers provided kinetic data, which enabled our team to size the reactor more efficiently and to monitor reaction rates. We assumed power law kinetics governed the system, in order to understand the catalyst and its influence on the reaction rate. Chevron provided our team with cascade controllers and PID (proportional-integral-derivative) controllers for measuring the necessary parameters. Chevron gave Mr. Karpay specific production targets to create grade AA methanol. The methanol production target was 500 mol/hr with a reactor temperature no greater than 610K.

III. Theory

The following two reactions are used in industry to make gaseous methanol:

(1) Fischer-Tropsch reaction[1]: $CO_{(g)} + 2H_{2(g)} \Leftrightarrow CH_3OH_{(g)}$

(2) Water Shift Reaction[2]: $CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$

The first reaction occurs in the methanol reactor, while the second reaction is an alternative. The kinetic rate law, which our team assumed to be written in the power law form[3], is as follows:

$$-r_A = k(C_{CO})^{\alpha}(C_{H_2})^{\beta}(C_{CH_3OH})^{\gamma}$$

where k (/s) is the specific reaction rate constant, the powers of alpha, beta, and gamma are the reaction order for each species (usually ranging from 0 to 2) and $-r_A$ (mol/L· s) is the observed reaction rate. Also, $-r_A = [k(T)][fn(C_{CO}, C_{H_2}, \ldots]$[3] and the species concentration $C_j = h(X)$ are both a function of the conversion, X. Notice that the overall reaction rate is a function of temperature, concentration, and conversion.

IV. Process Improvement

There are three viable alternatives to optimize this methanol reactor. These optimization schemes are as follows:

1. Increasing the concentration of natural gas, by increasing flow rates, will increase conversion rates and methanol production.
2. Resizing the reactor at a fixed temperature can significantly improve conversion and methanol production.
3. Increasing reactor temperature just below the catalyst degradation temperature of 610 K will improve the kinetics thereby increasing the conversion of methanol and its production.

Increasing the concentration of natural gas will result in an increase in conversion rates for a given reactor volume. From the equations given in the theory section, increasing the feed concentration will increase the reaction rate. We know the reaction order is important in this case, since it will determine how sensitive the reaction rate is with concentration.

Resizing the methanol reactor will involve the kinetic rate law expression (see Theory section). In reactor design, one governing principle is that to achieve a higher conversion more reactor volume is needed[3]. So a higher production target implies a higher conversion and, therefore, a larger required reactor volume.

Increasing the temperature of the reactor or the reaction itself is the simplest pathway. We know the catalyst can withstand temperatures up to 610K according to our catalyst suppliers. Neglecting pressure drops in the reactor, and increasing the reactor temperature, will increase or speed up the reaction. The reaction occurring in the reactor is very exothermic and must be handled carefully. Using both cascade and PID controllers, increasing the temperature will result in higher conversions since the reaction rate increases for a fixed volume.

V. Equipment

PID Controllers[4]*:*

According to the manufacturer, "These controllers compare a measured value from a process with a reference set point value. The difference or 'error' signal is then processed to calculate a new value for a manipulated process input, which . . . then brings the process-measured value back to its desired set point. The PID controller can adjust process inputs based on the history and rate of change of the error signal, which gives more accurate and stable control. It can be shown mathematically that a PID loop will produce accurate stable control in cases where other control algorithms will either have a steady-state error or will cause the process to oscillate."

Cascade Controllers[5]*:*

According to the Invensys Eurotherm website, "Cascade control is used to enable a process having multiple lags to be controlled with the fastest possible response to process disturbances including set point changes. Here you control a secondary, more responsive process that lies within the overall loop and influences the main process."

VI. Evaluation Procedure

The first optimization scheme dealt with feed flow rates and concentration dependence. The flow rate of natural gas was varied across a range of roughly 700 mol/hr to 900 mol/hr. Changing the flow rates of natural gas altered the reaction rate in the reactor by changing natural gas concentrations. The PID controllers controlled the flow rates and measured key reaction parameters. The flow rates were measured every hour and a database was collected. Using software packages provided by Mr. Karpay, the data collected was analyzed and results were reported.

The PID controllers were also used to change and measure reactor temperatures. These temperatures fluctuated from 450K to 670K over a one-day period. As a result, the reaction rate was known as a function of both feed flow rate and temperature. Recall that pressure drops in the reactor were neglected. Upstream processing units were installed to accommodate any pressure changes of the streams coming into and out of the reactor.

The collected data was further analyzed and the reaction rate was clearly dependent upon feed flow rates and temperature. Further analysis was done using Process Design simulation software. The conversion of the reactor was investigated as a function of reactor volume, temperature, and feed flow rates. Methanol flow rates were also collected throughout the day. Maintenance costs and other costs were determined from simulation software.

The nominal Operating time frame was 330 days/year. Eleven economic cost calculations were performed across various operating conditions including both heat management and maintenance costs. The collected data represented reaction rate as a function of conversion, temperature, reactor volume, and economic cost.

VII. Results

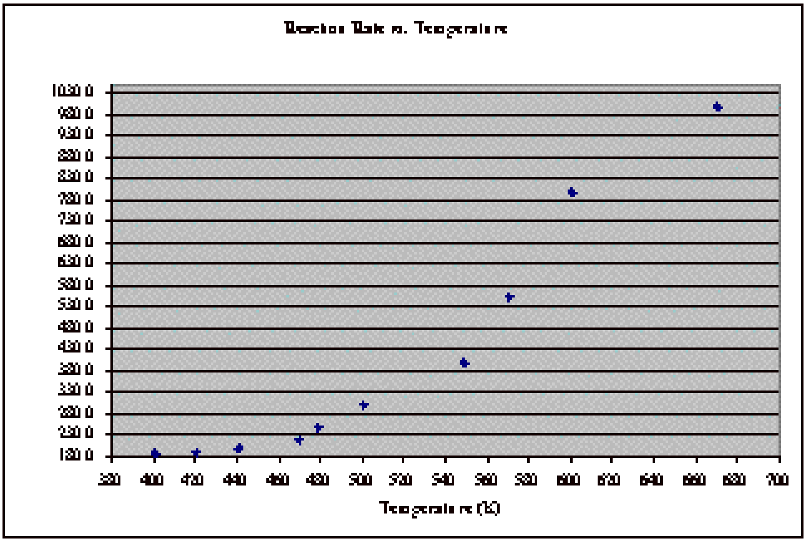


Figure 1: Inverse Reaction Rate as a function of Temperature
Note: The inverse of the reaction rate was plotted instead of the reaction rate. This was based on chemical reaction engineering principles.

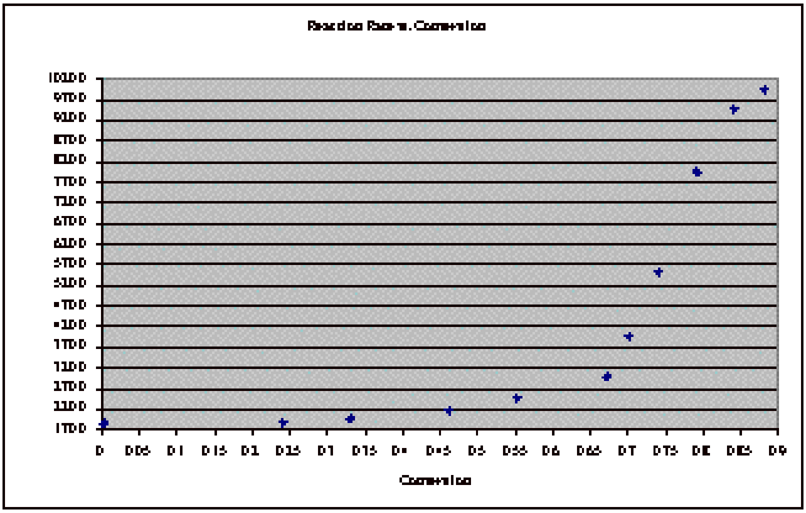


Figure 2: Inverse Reaction Rate as a function of Conversion
Note: The area under the curve gives the reactor volume necessary for a desired conversion. Higher conversion implies a larger required reactor volume.

Table 1: Economic Costs under different operating conditions

Note: These costs incorporate maintenance and utilities costs. The maximum attainable conversion was 0.88 or 88%. The abbreviation M is millions of dollars. Costs were based on reactor operation only.

Cost ($ MM/ yr)	Pressure (MPa)	Conversion	Temperature (K)	Volume (L)	Feed flow rate (mol/hr)	Methanol rate (mol/hr)
9.2	7	0.002	400	0.393	700	360
16.5	7	0.24	420	8.54	720	375
18.3	7	0.33	440	28.0	745	380
19.4	7	0.46	469	59.6	789	395
20.4	7	0.55	478	77.3	810	410
20.6	7	0.67	500	106.8	844	432
22.7	7	0.7	548	118.4	857	448
23.4	7	0.74	570	138.3	865	468
24.9	7	0.79	600	171.3	888	500
25.6	7	0.84	650	213.6	894	523
27.3	7	0.88	670	253	900	566

VIII. Conclusions & Recommendations

THE MOST RELEVANT data collected from the PID controller was that of reaction rate as a function of temperature and conversion. As the temperature in the reactor increased, the reaction rate increased and produced higher conversions of methanol. Pressure had little influence on the reaction rate, as shown in Table 1. However, as the reaction rate increased, the reactor volume necessary also increased. The maximum conversion was 88% with a volume of 253 L (Figure 2). Yet Chevron must consider the most feasible pathway with regards to economic costs *and* methanol output.

The most attractive optimization scheme is at the conversion of 79% (see Table 1). The catalyst used in the reactor degrades at 610K and any reactor temperature above 610K will destroy the catalyst. At 600K, we observe an overall cost of $24.9M/yr with a required reactor volume of 171.3 Liters. The most viable alternative for optimizing this reactor is to simply increase its temperature just below that of the catalyst degradation temperature of 610K. Notice that at 79% conversion, methanol production is exactly 500 mol/hr, which is our production target.

Using temperature and volume we can dictate the appropriate conversion of methanol. Our competitors have only been able to achieve 70% conversion. Using the already mentioned scheme, we can achieve more. The natural gas flow rate at 79% conversion is 888 mol/hr, which is roughly 14,236 g/hr or 14.2 kg/hr and this can easily be supplied. In general, a feasible route for optimizing the methanol reactor requires finding a reactor temperature that can achieve the highest conversion, while, at the same time, including reasonable reactor volume, satisfying the methanol production target, and not degrading the catalyst being used.

Therefore, using both PID and Cascade controller devices, both monitoring the performance of the reactor under various operating conditions, yielded the best results with little variation at 79% conversion. Overall, the third alternative is the most productive for achieving both the requested production target of 500 mol/hr and a conversion over 65%.

Mr. Karpay helped us greatly in optimizing this reactor by providing data and software. We now have demonstrated that the methanol reactor can be optimized at a minimal cost, with the highest conversion, with a reasonable reactor temperature, and with preservation of the present catalyst.

In sum, Chevron has the opportunity to produce grade AA methanol and to enhance methanol's applicability in the chemical industry. Chevron can now expand its research and development sector into making fuel cells and using its methanol to power them. Fuel is an asset that humanity cannot take for granted. Realizing this, Chevron is currently using all of its resources to generate energy for future vehicles that will promote a cleaner environment.

IX. References

[1] W.H. Cheng and H.H. Kung, *Methanol Production and Use*. New York: Marcel Dekker Inc., 1994.

[2] P.J.A. Tijm, F.J. Waller, and D.M. Brown, "Applied Catalysis," *Methanol technology developments for the new millennium*, vol. 221, pp. 275-82, 2001.

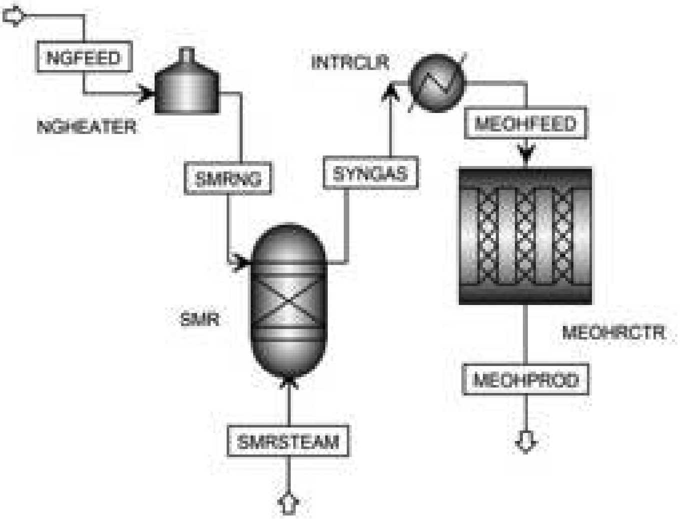
[3] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 3rd ed. New Jersey: Prentice Hall PTR, 1999.

[4] "PID Controller," Wikipedia on-line dictionary. http://en.wikipedia.org/wiki/PID_controller. Accessed May 6, 2006.

[5] "Cascade Controllers," Invensys Eurotherm company website. http://www.eurotherm.com.au/applic/applic_c/ t24_cascade.htm. Accessed May 7, 2006.

X. Appendix

Methanol Plant Flowsheet



Note: Figure originally prepared for paper entitled "Methanol production in Trinidad and Tobago," for ECH 158C: Plant Design, by authors E. Amirkhas, R. Bedi, S. Harley, and T. Lango.

Raw Data

“$-r_A$” (mol/L*s)	Temperature (K)	“$1/-r_A$” (L*s/mol)	Pressure (MPa)	Conversion
0.0053	400	188.68	7	0.002
0.0052	420	192.31	7.5	0.24
0.005	440	200.00	8	0.33
0.0045	469	222.22	8.5	0.46
0.004	478	250.00	9	0.55
0.0033	500	303.03	9.5	0.67
0.0025	548	400.00	10	0.7
0.0018	570	555.56	10.5	0.74
0.00125	600	800.00	10.85	0.79
0.00105	650	952.38	11.1	0.84
0.001	670	1000.00	12	0.88