1958

PROBLEM

TO THE CONTESTANT:

Process-design engineers are often given assignments similar to this problem. A preliminary evaluation of any process must be made in a specified time. The engineer given the job is expected to use good judgment in assessing the data and the process and in apportioning his time to the best advantage. He is also expected to present the results of his work in report form. The report must contain a summary for management and in a separate section must also show in some detail how the conclusions were reached. Clarity, accuracy, and good organization of the report are all important.

The subject of the 1958 problem is the economic process design of a plant to manufacture acetic anhydride from glacial acetic acid and acetone. The manufacturing concern does not know very much about the process and needs a preliminary evaluation. The engineering staff has already given the matter some thought and has suggested a flow scheme but has not had time to make a detailed study. The executive committee of the company has set the economic return which the anhydride plant must have to be of interest. At the present time the feasibility of the process, and of any suggested modifications, needs substantiation. A memorandum and two conferences give you, the new engineer, your assignment.

MANY CHEMICALS COMPANY

MEMORANDUM

To: Mr. A. Z. Newman

From: F. Older

Subject: Preliminary Evaluation of Proposal to Manufacture Acetic Anhydride

At our Millville plant we have for several years been using purchased acetic anhydride as one of the feeds to our Fixit unit. We also make both glacial acetic acid and acetone at Millville. A combination of recent production and sales trends leads us to consider using these latter two products to manufacture acetic anhydride instead of purchasing it. This can be done by making ketene from the acetone, and then reacting the ketene with glacial acetic acid to form the desired anhydride.

Will you please evaluate the desirability of manufacturing the anhydride versus purchasing it? The evaluation can be only preliminary, since we have practically no experimental data on the suggested process and must at present rely almost entirely on data from patents and the technical literature. In fact, the major purpose of the evaluation is to show us whether or not we should embark upon an experimental study of the process. But in any event we shall want to know the estimated cost of acetic anhydride made by the proposed process.

I realize that you have been with us for only a short time and that you will need some advice in carrying out this assignment. I suggest that you consult Jack Minor and Frank Major regarding the process and Ed Axis about the cost figures.

When you complete your evaluation, please send me a report giving your conclusions and the reasons for them. Be sure to append your detailed calculations.

F. Older
Chief Process Engineer

CONFERENCE NOTES

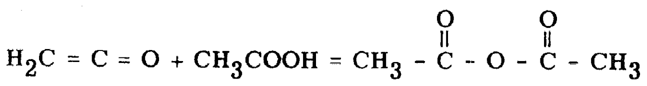
Present: F. X. Major, J. Y. Minor,
A. Z. Newman

Mr. Major: Fred Older tells me, Art, that you will be evaluating the acetic anhydride proposal for us. Don't let this throw you. The process is pretty straightforward, but will give you an unusual opportunity to show what you can do. Ordinarily you would have more direct supervision, but right now we are a little short-handed. You already know the essential feature of the problem: should we make acetic anhydride, or should we continue to buy it? This question can be answered only tentatively, since we don't yet have much process information. We shall want to make 1,150,000 lb. of anhydride/calendar month. Jack, will you tell Art what he needs to know about the chemistry involved?

Mr. Minor: I'll make a start. We know that acetone decomposes at high temperature to form ketene and methane and that some of the ketene then decomposes to form other materials.

Mr. Newman: I hate to show my ignorance, but what is ketene?

Mr. Minor: Ketene is $H_2C = C = O$. It is very reactive. The reaction that we want to occur here is



$$H_2C = C = O + CH_3COOH = CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$

ketene | glacial acetic acid | acetic anhydride

This reaction occurs very rapidly and completely when ketene is brought into contact with glacial acetic acid under suitable conditions. But if either the temperature or the acid concentration is too low the reaction is slow. So we think this reaction ought to be carried out at 80°C. or above, and with the acetic acid present at 50 mole % or greater in the reacting liquid. Also, we shall have to be careful to keep water out of the system, because ketene reacts with it to form acetic acid, which is not what we want to make.

Mr. Newman: Could we get back for a minute to the formation of ketene? I'm not clear on just how you want to do it.

Mr. Major: We'll feed liquid acetone to a gas-fired furnace. The acetone will be in pipes which will be heated by the hot gas. As a result, the acetone will be vaporized and then quickly heated to reaction temperature. For present purposes we shall assume that the best reaction temperature is 700°C. and that this is the temperature at the outlet of the transfer line.

Mr. Newman: Transfer line?

Mr. Major: That's the pipe that transfers the reacting gas from the furnace to the next step in the process. In this case the next step is a quench. We'll talk about that later. I'm just saying that the gas is at 700°C. when it enters the quench. I'd better tell you now that we aren't going to expect you to design the pyrolysis furnace. So for present purposes the furnace is a box into which we put acetone and heat and out of which we get reaction products and unreacted acetone at 700°C. You can take the furnace efficiency to be 65%. You can get the composition of the gas out of the furnace from this plot of yield versus conversion per pass (Figure 1). We know this isn't very accurate, since it's based on skimpy data in the literature plus one lab run that Jack made, but we are going to have to use it, because management is eager to get your preliminary evaluation as soon as possible.

Mr. Newman: I'm afraid you have lost me. Just what do you mean by yield and by conversion per pass?

Mr. Major: A very good question. Those terms are often used much too loosely. They ought always to be defined exactly. Conversion per pass is equal to (acetone reacted per unit time) divided by (acetone fed to the pyrolysis furnace per unit time). Yield is equal to (net moles of ketene formed per unit time) divided by (moles of acetone reacted per unit time). If we express this as a percentage, then 100 - yield = percentage of reacted acetone that forms side products. It will be accurate enough to say that these side products are 67% CO and 33% C_2H_4, by volume. We know that a little elementary carbon is formed, too. But you should neglect it. The same is true of tar. Ketene can polymerize and otherwise react to form tars. We are just going to be optimistic about that and neglect the formation of such side products. Anyhow, we have some reason to believe that small portions of such materials will not be objectionable in the product anhydride. Remember, we're not making anhydride for sale, but just for use in our own Fixit unit. From consideration of Fixit requirements we think the only significant spec on the anhydride is that it should contain no more than 0.15% acetic acid by weight. But let's get back for a moment to the tars. We are sure that the higher the pyrolysis pressure, the greater the tendency of ketene to form undesirable side products. We believe that the yields in the diagram can be obtained at about atmospheric pressure on the pyrolysis - at least we'll assume so. But we definitely should operate so that the pressure at the pyrolyzer outlet is no higher than necessary. So let's take the quench inlet pressure to be 3 lb. gauge.

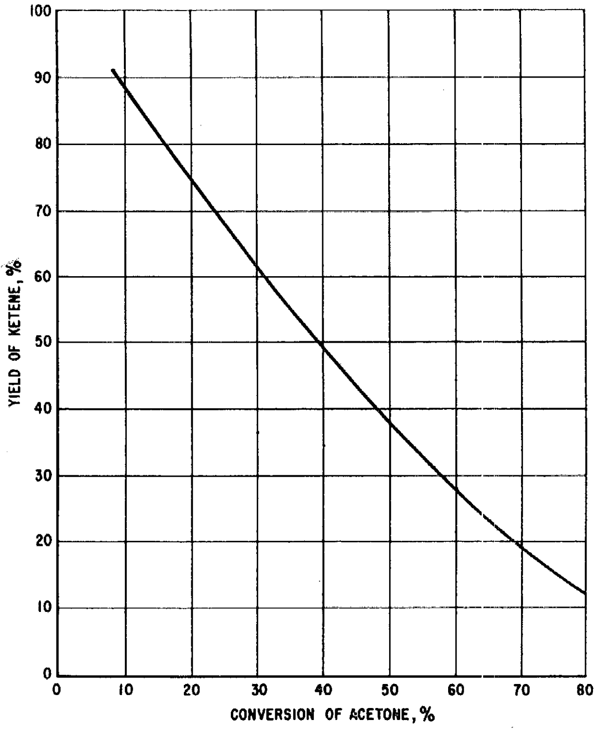


Fig. 1. Ketene yield vs. acetone conversion per pass.

Mr. Newman: What conversion shall I use?

Mr. Major: That is something you will have to tell us. But I think it will turn out to be fairly small.

Mr. Newman: You mentioned the ketene reactor and the quench. Have you thought about the rest of the process?

Mr. Major: Yes, somewhat. Here's an outline of the flow scheme that we think you should investigate (Figure 2). I should like to emphasize that this is only an outline. Besides, you may be able to make some minor modifications that would improve the economy of the process. If you think of an improvement you should incorporate it. But remember that we want to know why it is an improvement.

Mr. Newman: Before we get into this discussion any further, will you tell me what order of accuracy I should use in making my calculations?

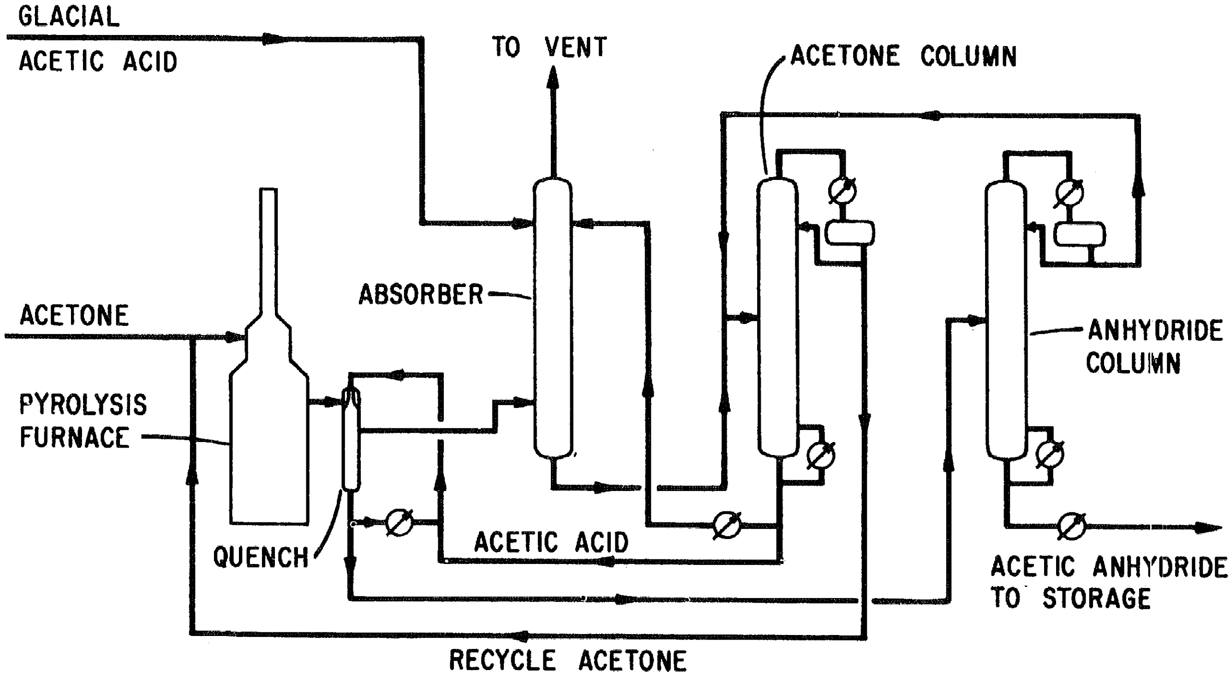


Fig. 2. Suggested flow diagram: acetic anhydride plant.

Mr. Major: O. K. That's a good point. By and large, great accuracy is certainly not indicated. The whole process is too uncertain for that. But you will have to use your own judgment. There may be parts of the process where fairly accurate calculations are needed, so as to see whether or not the suggested operation is feasible. I'll give you a few additional points as we discuss the flow sheet. Is that enough for now?

Mr. Newman: I guess so, but I admit I'm still in a bit of a fog.

Mr. Major: That will clear up when you have time to sit down and consider the process carefully. As you can see, the pyrolysis products enter an injector, where they contact a circulating stream of liquid and thus are rapidly quenched.

Mr. Newman: Quenching means cooling. Is that right?

Mr. Major: Yes, rapid cooling. We are going to assume that two things happen in this quenching operation: first, rapid cooling and, second, complete reaction of the ketene with acetic acid. We know this isn't exactly true, but we think it isn't far wrong. Besides, the unreacted ketene will have additional time for reaction in the absorber and the anhydride column. To get the ketene to react with sufficient speed we shall have to have sufficiently high levels of temperature and of acetic acid concentration in the exit liquid from the quench. We don't have much basis for this, but to be definite let's say that this liquid must be at 80°C. or above and must contain at least 50 mole % acetic acid.

The gas from the quench goes to an absorber, where acetic acid is the absorbing liquid. This is a physical absorption. Incidentally, I think you will have to give the absorption step pretty careful attention. The acetic acid flow rate probably shouldn't be much above the minimum. The minimum L/V will probably be determined by conditions at the bottom of the absorber. The vent gas should contain not more than 1/4 mole % acetone.

The absorber bottoms go to a distillation column which takes acetone overhead. The bottoms are recycled to the absorber.

Mr. Newman: You said that a little ketene might get into the absorber. I suppose it would react there with the acid. What happens to the acetic anhydride that it forms?

Mr. Major: Some of this anhydride would go out through the quench. But for present purposes we shall assume that no anhydride or other nonvolatile material forms in the absorption and distillation system. Anyhow, I don't think too much harm would be done by a little anhydride. If we have to, we can clean up the recirculating acid in some equipment that is already available, or we can take off a small stream to the anhydride column. Just neglect this in your calculations. We will of course bear this point in mind for future investigation if your work indicates that the process is attractive.

The acetone for recycle should contain very little acetic acid. The reason is that acetic acid pyrolyzes to form ketene and water. These would recombine to form acetic acid in the quench system. This would make the cooling load greater and might lead to other complications. To be reasonably safe, let's say that the acetone for recycle contains 1/4 mole % acetic acid.

The liquid from the quench goes to the anhydride column. The bottom product from this column is acetic anhydride ready for use in our Fixit plant. The top product is returned to the acetone column. Oh, by the way, Art, did you have anything in college on multicomponent distillation?

Mr. Newman: Nothing to speak of.

Mr. Major: That poses a small problem. There are three components in the anhydride column, but I think we can treat it like a binary with enough accuracy. In calculating the plate requirements, take both of the top product components to be acetic acid. But do not use this assumption for any other purpose.

Mr. Newman: Can you tell me where to get the physical-properties data that I'll need?

Mr. Major: You can find nearly all that you will need in the literature. For example, you will find x, y data for the acetone - acetic acid system at one atmosphere. For conditions other than those covered by the literature, assume for now that the activity coefficients depend on composition only. Do you check me on that, Jack?

Mr. Minor: I think that assumption will be good enough.

Mr. Newman: I'm a little rusty on activity coefficients. Will you go over that again?

Mr. Minor: All we mean by activity coefficients is the ratio of vapor-liquid K to the Raoult's Law value of K.

Mr. Newman: By K you mean the equilibrium value of y over x?

Mr. Major: Yes. Also, I don't think I mentioned that atmospheric pressure will be all right for the distillations.

Mr. Minor: I might as well give you the literature references for vapor-liquid equilibria. You can find acetone, acetic acid, and acetic acid - acetic anhydride in Ju Chin Chu. The original reference for acetone - acetic acid is D. F. Othmer, Ind. Eng. Chem., 35, 614 (1943). Also, Brown gives some smoothed data. The acetic acid - acetic anhydride data were obtained by K. P. Miscenko and S. J. Tscherbov. There are two references here. One is J. Russ. Phys. Chem. Soc., Chem. Part 2, 1509 (1930); the other is Z. physik. Chem., 148A, 386 (1930).

Mr. Newman: You haven't mentioned materials of construction yet.

Mr. Major: No, I was just coming to that. Use aluminum throughout. Actually, type-446 stainless will be used for the pyrolysis, but its cost will be included in the furnace costs we'll give you; so it won't enter as a separate item. You can get most of your capital costs from Aries and Newton's book. I think you will find that on our reserved-book shelf. I had better give you some more information on the quench equipment, however. Here are the costs for mild-steel quenchers. You will have to adjust this to correspond to aluminum.

Mr. Minor: Didn't you tell me, Frank, that the quencher would be a relatively inexpensive item?

Mr. Major: That's right, I did. The gas-liquid contactor, that is. So a flat cost for the contactor will probably be adequate. Check with Ed Axis, Art.

Mr. Minor: You will need a couple of other items of physical data, Art. Take the specific heat of gaseous acetone to be 0.36 + 0.00063t cal./(g.)(^{o}C.) up to 275^{o}C. and 0.42 + 0.00041t between 275^{o} and 700^{o}C., where t is in ^{o}C. Take c_p of liquid acetic anhydride to be 0.55 cal./(g.)(^{o}C.). Take the heat of reaction for ketene formation to be 19,000 cal. absorbed/g.-mole of acetone reacted. For ketene decomposition take the heat of reaction to be 15,000 cal. evolved/g.-mole of ketene decomposed. These are values that we estimated for 700^{o}C. In the reaction of ketene with acetic acid, 11,500 cal. are evolved per gram-mole of anhydride formed.

Mr. Newman: You said I should use my own judgment in regard to accuracy. I've been thinking that approximate, over-all U values will be good enough. Is that right?

Mr. Major: Yes. While we are on the subject, let's set some values of U. Take U = 75 for reboilers, 100 for coolers, and 150 for total condensers. Those are in English units. Also, I had better tell you to take the cooling-water temperature to be 30^{o}C. Use a 15^{o}C. rise on the water.

For heating, we have two steam systems. One is at 150 lb. and the other at 400 lb. Those are gauge pressures.

Mr. Newman: Saturated steam?

Mr. Major: Yes.

Mr. Newman: What's a reasonable pressure drop across the pyrolysis reactor?

Mr. Major: Just use a 100-lb. drop between furnace inlet and quench inlet. That will do for this purpose. Probably this is high, but use it. I think we have covered all that we need to go into, except for one item. The Fixit plant runs continuously for considerable periods of time, but occasionally may be down for as much as a week at a time. Let's assume that our anhydride plant will be on stream 680 hr./month. I think that about covers all you will need to know, except for what Ed Axis will tell you. Agreed?

Mr. Newman: I guess so. It looks pretty straightforward now. But I would like to know what patent was referred to.

Mr. Major: U. S. Patent 2,509,877.

CONFERENCE NOTES

Present: J. P. Axis, A. Z. Newman

Mr. Axis: This early-stage evaluation of the acetic anhydride proposal is of considerable interest to our management, Art.

Mr. Newman: Yes, I understand that. Mr. Older indicated you could fill me in on the economic factors to consider.

Mr. Axis: Well, first, let's consider our approach. If our company goes ahead with this project it will be necessary to build a plant for 1,150,000 lb. of acetic anhydride a month when the plant is operating at capacity. This would involve spending a considerable amount of money for equipment and plant construction. This would be our investment or capital outlay. To operate the plant we'd have to spend money for raw materials, utilities, operating labor, and other costs that go along with making an investment. These other costs are those for depreciation, maintenance, and insurance. To justify these expenditures, our company would have to receive some profit. Annual dollar profit divided by the investment required for the acetic anhydride plant is referred to as "return on capital." We express this as a percentage. Now, our executive committee have considered very briefly the acetic anhydride problem. They have set a minimum return on investment that would be required before they would be interested in going ahead with the project. Of course you probably realize that this minimum level of return is a result of considering many factors. They would be interested in this project if the return on the plant capital were above 22%.

Mr. Newman: How about taxes charged by the Federal Government on corporation incomes?

Mr. Axis: The 22% figure stands for the return before any payments are made for this tax. There is one thing you should realize. We use certain financial yardsticks for evaluations within MANY. Other yardsticks could be used, but consistency in evaluations is essential. Studies on consistent bases can be thought about and converted to other bases by our management.

In your problem you should be concerned with the return on the plant capital before taxes. This should be figured for the plant operating at capacity. I have tabulated the values you should use for raw materials and utilities. We should consider the acetone and acetic acid used in your plant at values about the same as the market prices for these materials. Since your production of acetic anhydride will eliminate purchasing the material, at $0.14/lb., for our Fixit unit, your product would be worth $0.14/lb. of acetic anhydride.

I believe the following information will help you.

Cost Items

Acetone	$0.07/lb.
Glacial acetic acid	$0.09/lb.
150-lb. steam	$0.30/1,000 lb.
Power	$0.01/kw.-hr.
Cooling water	$0.02/1,000 gal.
Fuel gas	$0.25/million B.t.u. content
Operating labor	$0.005/lb. of product
Depreciation, maintenance, and insurance	17.5% of plant capital/year

Capital Items

General:

Use Aries and Newton, "Chemical Engineering Cost Estimation," McGraw-Hill Book Company, Inc. (1955), for estimating purchased-equipment cost. Use an escalation factor of 1.22 to convert from 1954 costs to present costs.

Furnaces:

Heat absorbed, millions B.t.u./hr.	Purchased cost of furnace, present cost
2.0	$18,500
10.0	$46,500
20.0	$75,000

Scrubber (quench):
Use purchased-equipment cost of $3,000 for any designs considered (present cost).

Heat exchangers:
Multiply the purchased cost for steel shell-and-tube exchangers by 2.0 to convert to cost for exchangers with aluminum tubes.

Pumps:
Multiply the purchased cost for steel pumps by 1.3 to convert to cost for aluminum pumps.

Purchased-equipment cost should be multiplied by 4.0 to arrive at the total installed-plant cost. This should be done for any design considered. Purchased equipment includes

> Furnaces, shell-and-tube equipment, towers, the scrubber, pumps and motor drivers, drums, and tankage. The factor of 4 covers installation, piping, instrumentation, electrical work, building, engineering, construction fees, and contingencies.

Mr. Newman: You gave several factors based on plant capital. Did you always mean total installed cost of the plant?

Mr. Axis: Yes. Are you all set now?

Mr. Newman: Yes. I think I'm ready to go to work now.