Introduction

The basic purpose of chemical industry is to convert raw materials into useful products for the society. For example, crude oil sourced from oil reservoirs cannot be used as it is. Refineries convert the crude oil, through several chemical and physical processes, into products that we use in our daily life. Petrol, diesel, lube oils, LPG are a few products of the refineries. There are about 10 basic raw materials such as oil, natural gas, coal, available in nature. These are converted base chemicals, which are then transformed to intermediate chemicals. Final products are made from the based and intermediate chemicals. Below Figure shows chemical industry “tree.”

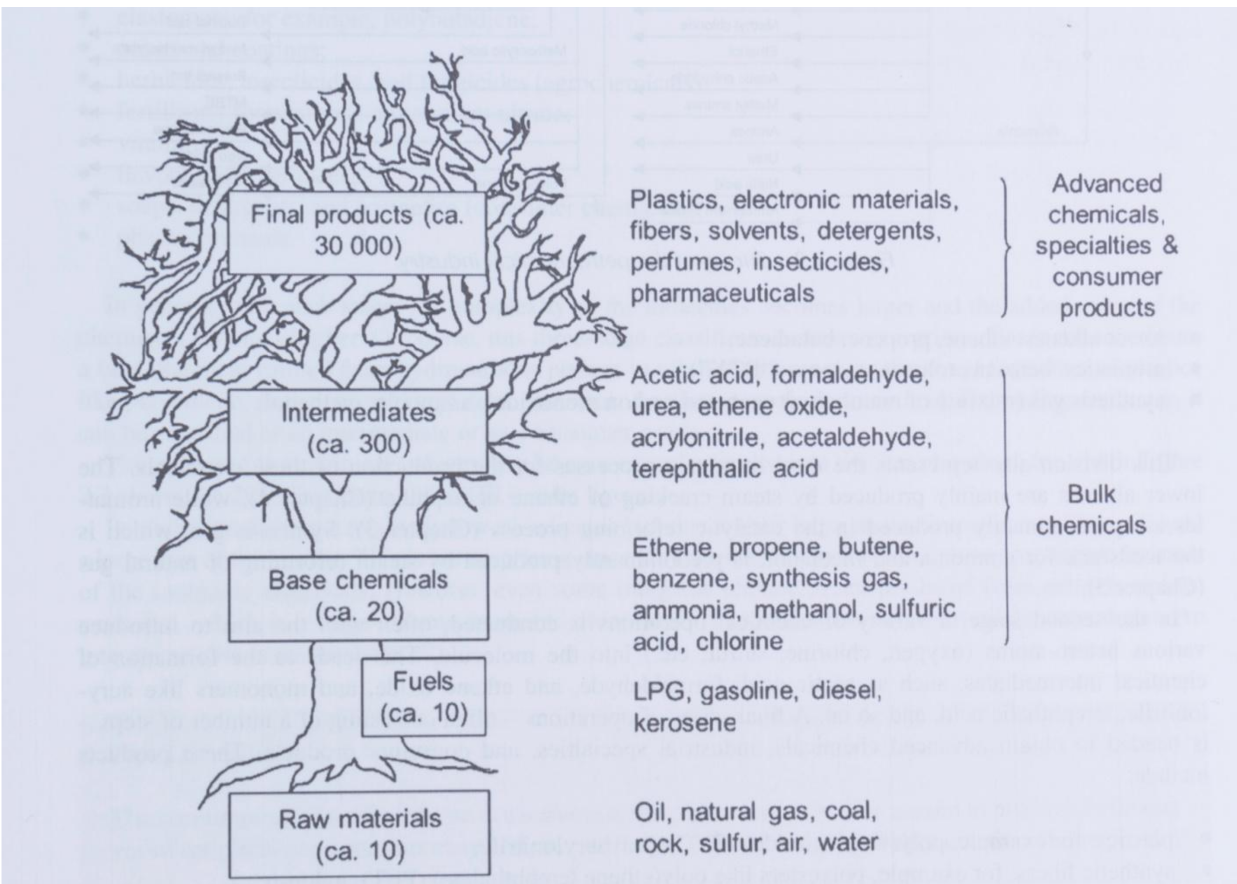
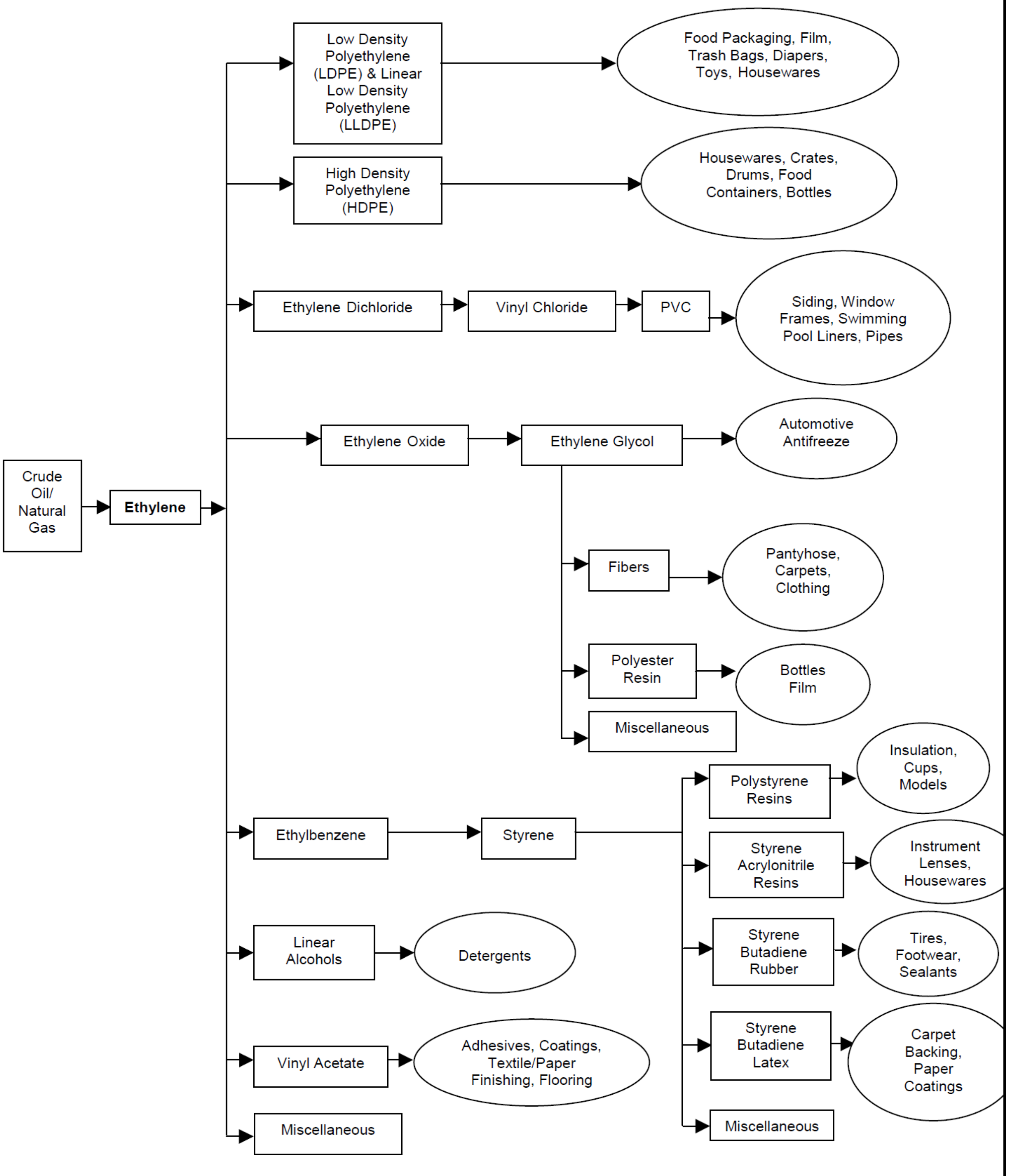


Figure 2.1 *Structure of the chemical industry.*

Adapted: Chemical Process Technology, Moulijn et al., 2nd ed, 2013

Ethylene Chain

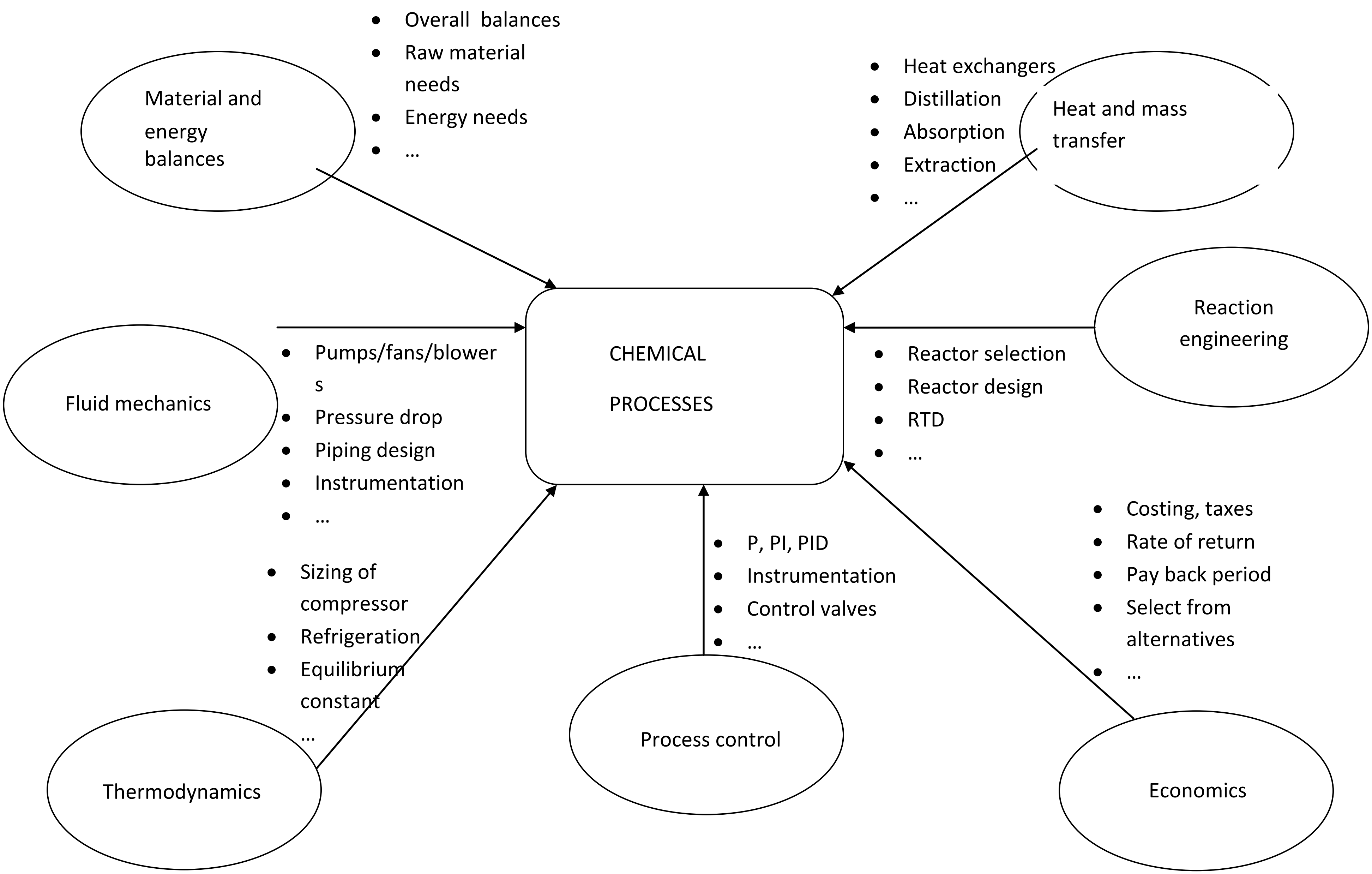


Bulk chemicals are manufactured by continuous processes; fine chemicals, specialty chemicals and pharmaceuticals are often made by batch processes due to low volumes of production, seasonal requirements and flexibility to make several products. The continuous processes are easier to control than batch processes because the former operate at steady state; the former are more economical than the latter due to economies of scale. Table below shows the bulk and fine chemicals manufactured.

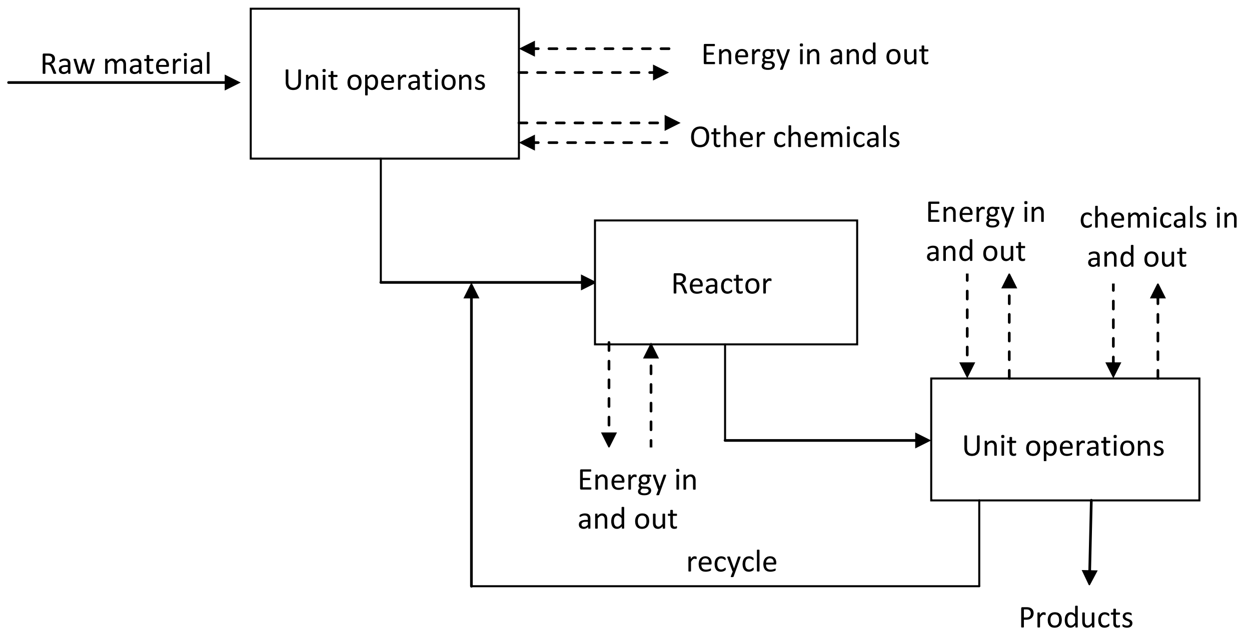
Bulk chemicals		**Fine and specialty chemicals pharmaceuticals**	
Chemical	*Production in kg/year*	*Chemical*	*Production in kg/year*
Sulfuric Acid	3.25×10^{11}	α-interferon	~10
Ethane	2.4×10^{11}	Streptokinase	~10
Propane	1.4×10^{11}	Insulin	~10^{4}
Chlorine	9.7×10^{10}	Penicillin	5×10^{7}

Chemical engineering/technology is orchestration of science [chemistry, physics and mathematics], engineering, economics, safety, environment to make a product from a raw material. As engineers, we need to ensure that raw materials and energy resources are conserved and not wasted (excessive use of raw materials and energy); pollution standards of the time are adhered to; quality of the products is maintained; safety of equipment and personnel is given due importance.

You have taken several core courses in chemical engineering curriculum such as material and energy balances, fluid mechanics, thermodynamics, reaction engineering, separation processes and economics. This course (CL 306: Chemical Processes) unifies all the previous courses, draws upon the fundamentals and applications learnt in those courses to develop a flowsheet to make a chemical from a given raw material. Figure in the next page shows connection between the core courses and CL 306.


Material and energy balances
Overall balances
Raw material needs
Energy needs
…
Heat and mass transfer
Heat exchangers
Distillation
Absorption
Extraction
…
Fluid mechanics
Pumps/fans/blowers
Pressure drop
Piping design
Instrumentation
…
CHEMICAL PROCESSES
Reaction engineering
Reactor selection
Reactor design
RTD
…
Thermodynamics
Sizing of compressor
Refrigeration
Equilibrium constant
…
Process control
P, PI, PID
Instrumentation
Control valves
…
Economics
Costing, taxes
Rate of return
Pay back period
Select from alternatives
…

General scheme for manufacture of a chemical



Production process for any bulk chemical (it is applicable for fine chemicals also) can be roughly divided into three sequential steps: raw material preparation, reaction and downstream separation. Usually raw materials are physically processed in one or several unit operations to make them suitable for reaction. Examples of physical treatment of raw material

- Coal needs to be pulverized for burning/ gasification
- Limestone is crushed and ground in cement manufacture
- H_2S is removed from natural gas
- Benzene is dehydrated before further processing to make ethylbenzene

The raw material is converted into product in a reactor. The reaction could be heterogeneous or homogeneous; exothermic or endothermic; liquid phase or vapour phase. In a typical chemical plant, reactor operates at high temperatures. As a result, side products are inevitably produced. Catalyst may improve selectivity toward the desirable component but will not eliminate side products. There are a few exceptions, however. Downstream of reactor, therefore, product is separated from the side-products in one or many unit operations (only physical separations happen, no chemical changes occur). Unreacted reactant(s) are recycled to the reactor to enhance conversion. Most of the production cost is due to raw materials.

Learning Outcomes for Sulphuric Acid Process

- Write all the chemical reactions for the process
- List the raw materials needed to make sulphuric acid commercially
- Explain why oxygen is supplied in the form of air and not as pure oxygen, even though nitrogen plays no part in the process
- Compare fixed bed reactor and shell-and-tube type reactors for oxidation of SO_2
- Draw a reactor configuration for achieving 99.7% conversion of SO_2 to SO_3 and explain how it works
- Explain the choice of pressure for the process; discuss the pros and cons of high and low pressures
- Draw a process flow diagram for the entire process and explain this diagram

Sulphuric Acid Process

Sulphuric acid is by far the largest volume chemical produced. For this reason, it is also called the king of chemicals. Major uses for sulphuric acid are in: manufacture of fertilizers, alkylation step in crude oil refining, copper leaching, making of lead-acid storage battery in motor vehicles as an electrolyte etc.

The reactions involved in the commercial manufacture of sulphuric acid are:

Oxidation of sulphur to SO_2

$$S\,(l) + O_2\,(g) \longrightarrow SO_2\,(g) \qquad \Delta H^o_{298} = -298.3\ {}^{kJ}/_{mol}$$

Oxidation of SO_2 to SO_3

$$SO_2\,(g) + 0.5\,O_2\,(g) \rightleftarrows SO_3\,(g) \qquad \Delta H^o_{298} = -98.5\ {}^{kJ}/_{mol}$$

Absorption of SO_3 to form H_2SO_4

$$SO_3\,(g) + H_2O\,(l) \longrightarrow H_2SO_4 \qquad \Delta H^o_{298} = -130.4\ {}^{kJ}/_{mol}$$

Sulphur is oxidized to SO_2 first; then, SO_2 is further oxidized to SO_3; the generated SO_3 is absorbed in water to produce H_2SO_4; if SO_3 is absorbed in H_2SO_4, oleum [$H_2S_2O_7$] is produced.

The raw materials needed for the production of H_2SO_4 are: ______________________________

How much sulphur is required to make 300 tons per day of H_2SO_4?

Sulphur is typically obtained from petroleum refineries where it is made from processing of crude oil. If sulphur content is < 0.5 wt %, the crude is called sweet; if it's between 1.0-2.0 wt %, it is termed sour; some crudes may have sulphur content > 4.0 wt % also.

Assuming 100 % conversion for the above reactions (reaction 2 can never go to 100 % completion, why?),

Draw a block diagram for the production of H_2SO_4. Block diagram shows the sequential arrangement of operations needed for the production of a chemical. Each block indicates one operation with inlet and outlet streams. Be sure to write the components of these streams in the diagram.

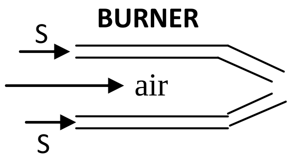
Let's study each of the blocks in detail starting with oxidation of sulphur. By this study we seek to get insights into the sulphuric acid process and draw a detailed block diagram later. The insights drawn here could help us with understanding of other chemical processes.

Sulphur oxidation

Refineries supply sulphur as a yellow solid. Sulphur is recovered from crude oil as hydrogen sulphide (H_2S) from which sulphur is produced.

Which of the below options is appropriate for oxidizing [burning] sulphur to SO_2? Think about pros and cons of each of the two options.

Option A: Grind it to fine powder, mix it with air.



Sulphur burns in air at the outlet of the burner to produce SO_2. Initial ignition is necessary. The flame sustains itself after the ignition.

Option B: Melt it by heating it 15 degrees above its melting point (115 ^oC), atomize it by passing the melt through a burner to produce small droplets of sulphur and then burn the droplets with air. Here 15 is arbitrary; it could be few degrees higher or lower. However, it cannot be too high.

Select an option for supply of O_2 to oxidize of sulphur. Again compare pros and cons of the two below options. Hint: think about O_2 separation from air, size of downstream equipment, if oxygen is separated etc.

Option A: O_2 through the supply of air

Option B: Pure O_2 after separating air into N_2 and O_2

Air Drying

Air used to burn sulphur and oxidize SO_2 to SO_3 needs to be bone dry (what's this? Find out). Rashtriya Chemical and Fertilizers (RCF) Limited, located in Chembur, Mumbai produces sulphuric acid. In the monsoon months of June-September, air in Mumbai is usually saturated with moisture.

List a few methods below to dehumidify air

At what temperature and pressure would air be dehumidified? Be qualitative not quantitative in your answer. Indicate high or low for temperature and pressure.

The bone dry air converts [oxidizes] molten sulphur to SO_2. Speculate the outlet temperature of the stream emerging from sulphur oxidizer. Remember: this reaction involves burning of sulphur and its conversion to SO_2 is complete.

Now, draw a detailed block diagram consisting of two units: absorption tower and sulphur oxidizer. Write the components of all inlet and outlet streams and the operating conditions of the units.

SO_2 oxidation

The next step in the process is catalytic oxidation of SO_2 to SO_3 according to the below reaction. The catalyst is vanadium pentoxide [V_2O_5] on an inert carrier or support such as silica/alumina. The carrier materials offer high surface area on which the catalyst is dispersed and deposited. Distributing the catalyst over the support enhances its activity by exposing its surface to the reactants.

$$SO_2\,(g) + 0.5\,O_2\,(g) \rightleftharpoons SO_3\,(g) \qquad \Delta H^o_{298} = -98.5\ {}^{kJ}/_{mol}$$

This reaction is reversible and exothermic. Consequently, conversion of SO_2 is limited by equilibrium. The reaction has certain limitations on temperature: it occurs at temperatures > 425 ^oC, below this temperature, the rates are negligible; temperatures > 620 ^oC are detrimental to the vanadium pentoxide [V_2O_5] catalyst.

Our goal for this oxidation is to obtain upwards of 99 % conversion to ensure that the raw material, sulphur dioxide, is completely utilized and exceedingly low levels of unreacted SO_2 are released into the atmosphere through the vent gas. Remember: SO_2 is a pollutant that can cause acid rain.

We wish to select a reactor and its configuration to achieve our goal factoring in the constraints elucidated above. Before this selection, let's understand the effect of temperature on the rate of reaction of SO_2 and its equilibrium conversion.

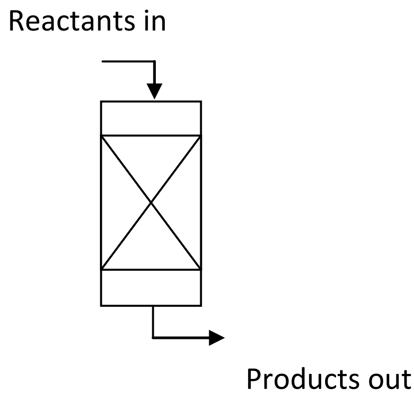
Recall Le Chatlier's principle for reversible and exothermic reactions.

According to Le Chatlier's principle, what temperatures and pressures favour high equilibrium conversion of SO_2? High or low? Explain. Be qualitative.

Draw the following graphs: i) equilibrium conversion of SO_2 oxidation versus temperature and ii) rate of forward reaction versus temperature. From these plots, identify and write the conflicting effects of temperature?

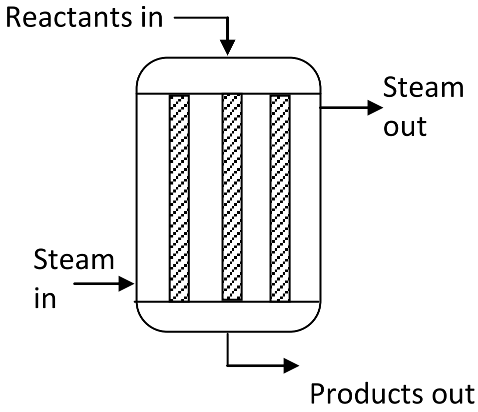
Now, let's discuss the features of different types of reactors used for heterogeneous systems. By heterogeneous here we mean reactants are in gaseous form that react on a solid catalyst. You might have studied these reactors in CL 324 course. After description of the features, we wish to discuss applicability of these reactors to oxidation of SO_2 to choose the best possible reactor to achieve our goals explained earlier.

i) Fixed bed reactor



Catalyst is dumped in reactor [cylindrical vessel] and held in place by a supporting plate at the bottom. The reactor is insulated so there is no heat exchange either with surroundings or with any coolant. If the reaction is exothermic, heat is released as the reactants traverse through the reactor. As this heat stays with reactants and the products, their temperature rises. As a consequence, the reaction rates rise leading to further increase in temperature of reactor contents. However, the reducing concentration of reactants lowers the rates, which eventually plateaus to a low value.

ii) Shell-and-tube-type reactor



Catalyst is filled in tubes measuring few inches in diameter. Such tubes are arranged as shown above. The reactants in the form of gas enter the tubes and react on the catalyst particles in the tubes. If the reactions are exothermic, heat is released as reaction proceeds. This heat is removed by circulating a coolant in the shell side, on the outside of the tubes. Typical coolant is water, which is converted to steam as it leaves the reactor. As heat is removed continuously, the reactor is operated under near-isothermal conditions. As the reaction progresses, the rates fall as the concentration of reaction decreases and temperature remains nearly same.

Compare features of fixed bed reactor and shell-and-tube type reactor configurations in a Table. Include temperature, rate, equilibrium conversion, ease of construction in your comparison.

Let's now generate a discussion on these reactors for the reaction, $SO_2 + 0.5\ O_2 \rightleftarrows SO_3$

Fixed bed reactors achieve high rates by allowing the temperature of reactor contents to rise. However, with rising temperatures, the equilibrium conversion that can be attained decreases. The reactor effluents exit the reactor at a higher temperature than the temperature at which they entered and an equilibrium conversion corresponding to this exit temperature. Clearly, this conversion is far less than 100 %.

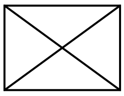
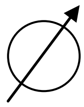
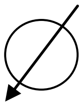
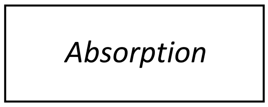
The equilibrium limitation on conversion of SO_2 is overcome by using multiple fixed bed reactors with interstage cooling. The stream emerging from the first bed is cooled and then passed through the second bed of catalyst. In this bed, the temperature rises again because of reaction. The effluent of second bed are cooled and then fed to the third bed.

As we keep using more beds of catalyst, SO_2 concentration keeps dropping after every bed and lowering the reaction rates. After three beds, the reaction is pushed forward by removing SO_3 by dissolving it in aqueous H_2SO_4 to produce concentrated H_2SO_4. The outlet stream of the absorber is passed through fourth bed to achieve an overall conversion of SO_2

upwards of 99 %. The effluents of this bed are passed through another absorber to mop up SO_3, again in aqueous H_2SO_4 to produce concentrated H_2SO_4.

Which reactor configuration is used to oxidize SO_2? What strategy is used to overcome the limitations of this configuration? Show the strategy on a plot of equilibrium conversion versus temperature and explain it.

Draw a flowchart that achieves 99.7 % conversion of SO_2 to SO_3. This flowchart should have four catalytic beds and two absorption towers. Include cooling and heating operations wherever necessary.

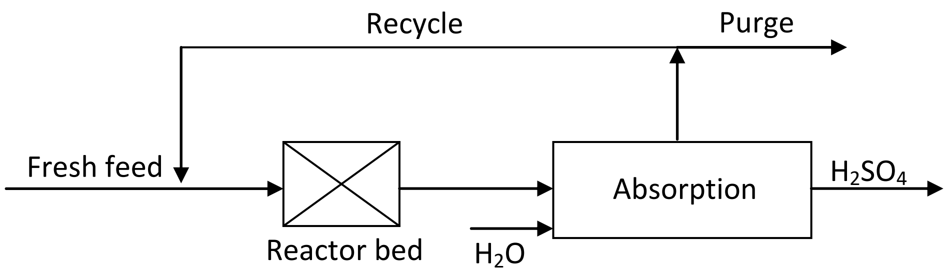
Use the following symbols for the flowchart:  *for fixed bed,*  *for cooler,*  *for heater and* 

for absorption tower

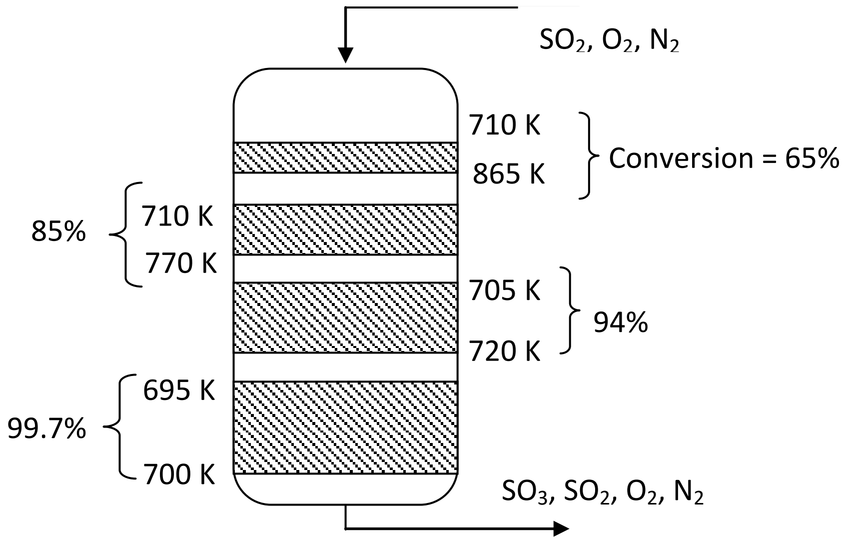
The sulphuric acid we discussed is called 'Double Contact Double Absorption [DCDA]' process because of two absorption towers and 'two contacts' with catalyst [first three beds is 'one' contact and the fourth bed is 'second' contact]

A friend of yours suggests a completely different idea to achieve high conversion of SO_2. The flowchart given below summarizes this idea. Give your opinion on this idea.

Idea: Effluents of reactor bed are separated, SO_3 is absorbed in water to form H_2SO_4, and unconverted SO_2 is recycled. To operate the process continuously a portion of the recycle stream is purged because the fresh feed stream contains N_2, an inert gas. Think: fraction of N_2 in the fresh feed stream and the fraction of recycle that needs to be purged. Can the challenge of 99.7% conversion be achieved with the purge?



A typical temperature profile in a four-bed SO_2 converter is shown below. Inter-stage cooling is not shown here.



In the previous question, you have drawn a flowchart for obtaining 99.7 % conversion for SO_2. This flowchart has coolers and heaters. Based on the flowchart and the values of conversion and temperatures indicated in the above figure, show that heat integration is possible in the flowchart. By heat integration, heat is exchanged between the available hot and cold streams without any adding any stream to the process to the extent possible. If heat is available after heat integration, this additional heat could be used to generate steam. If heat is needed after heat integration, an additional heat source is necessary.

Draw a detailed process flow diagram for the production of sulphuric acid using 'Double Contact Double Absorption' process.