Modeling of Reactor and Design for Styrene Production

A Dissertation

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By

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CERTIFICATE

This is to certify that the thesis entitled **"Modeling of Reactor and design for Styrene Production"** submitted by ***Adam stephen Talluri*** in partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Refining & Petrochemical Engineering**, at College of Engineering, University of Petroleum and Energy, is a record of the work carried out by him at University of Petroleum and Energy, Dehradun under my guidance and supervision.

To the best of my knowledge, the contents of this thesis did not form a basis of the award of any previous degree or published material by any one else.

The work is comprehensive of sufficient standard and here by recommended for the award of the degree of **M. Tech** in **Refining & Petrochemical Engineering**.

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AdamStephen 20/05/06

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ABSTRACT

Commercial development of styrene began during world war ii with the introduction synthetic rubber/ Butadiene-Styrene copolymers later found extensive use in latex paints while various polystyrene plastics and foams are used in packaging, wall tile, household articles, and insulating material in refrigerators . Styrene cab be produced via the catalytic dehydrogenation of methylbenzene, which is derived from the alkylation of benzene with ethylene. Precursor feedstocks are commonly associated with petroleum refining and petrochemical processes. Although the present supply and economics dictate the use of petroleum derived feedstocks a changing world situation could make coal-derived feedstocks acceptable alternatives. In either case , styrene in a valuable monomer in variety of commercial products.

The objective of this thesis work is to model of reactor and design for styrene production at 20 million pounds of styrene per year wenner and Dybdal (1) provided information on the reaction kinetics of the dehydrogenation of ethylbenzene. This information in designing the reactor. An O.D.E. solve (POLYMATH) is used to solved the mole balances, energy balance and momentum balance to find mole find the molarflowrates. Temperature and pressure of the system.

CHAPTER 1
INTRODUCTION

1.1 REACTANT AND PRODUCT INFORMATION:

Benzene is a colorless to light-yellow liquid with an aromatic odor. It is highly toxic with a tolerance of 25ppm in air. Benzene is derived from many sources, including distillation of coal tar and hydrodealkylation of toluene. It is used in industry as the building block for countless organic molecules and also as a solvent. Recent spot prices per metric ton of benzene were $392 in the US, $378 in Europe, and $420 in Asia. Benzene is within the 15 highest volume output chemicals in the US. Ethylbenzene is a colorless liquid with an aromatic odor. It is moderately toxic with a tolerance of 100ppm in air. Ethylbenzene is derived either by distillation of raw petroleum products, or by the heating of benzene and ethylene in the presence of aluminum chloride. It's only common industrial use is as an intermediate in the styrene production process. Recent spot prices for ethylbenzene were $473/mt in the US and $445/mt in Europe. Ethylbenzene is the 19th highest volume chemical produced in the US. Toluene, also known as methylbenzene, is a colorless liquid with a benzene-like odor. It is similarly toxic to ethylbenzene. It is also explosive in small parts with air, like styrene. The explosive limits are 1.27% to 7% in air. It is derived predominantly by distillation of coal-tar light oil. Toluene is used for many purposes from detergents to solvents to resins to a common organic reagent. Recent spot prices per metric ton for toluene were $310 in the US, $325 in Europe, and $340 in Asia. Styrene, our main product, is an oily colorless liquid with an aromatic odor. It is similarly toxic in air to ethylbenzene. A further danger of styrene is that its explosive limits in air are a mere 1.1% to 6.1% in air. Recent spot prices per metric ton for styrene were $601 in the US, $615 in Europe, and $662 in Asia. Styrene's main use is as the monomer for polystyrene, a common plastic. It is also a component of various resins and coatings.

1.2 REASONS FOR CHOOSING STYRENE AS THE PROJECT WORK:

Styrene plastics are easy to process and offer excellent price/performance ratios. Polystyrenes are used everywhere: as packaging materials or containers, and in a wide range of appliance and equipment housings. Polystyrene compounds are the fourth largest production plastics in use. Polystyrene is used in food packaging materials such as egg cartons, coffee cups, trays and other disposable products. Two styrene products commonly found in the home are styrofoam insulation panels and polystyrene vapor barriers. Styrene is co-polymerized with other materials to make products such as styrene butadiene rubber (SBR), acrylonitrile butadiene styrene plastics (ABS), styreneated alkyd coatings and as a reactive diluent in polyester/fiber glass products. Other co-polymers of styrene are used for adhesives, foams, coatings and rigid plastics. When polystyrene is burned it degrades to styrene which is a system toxin and benzene which is a toxin and carcinogen. As with most plastics, polystyrene compounds can out-gas and be broken down by UV causing them to release toxic materials.

Styrene polymers have evolved as more than commodity polystyrene. Even with ABS reaching commodity status with volumes over one billion pounds and prices in the $.80/lb. range, other styrene polymers have become successful and important commercial products. Styrene polymers have found use in almost every plastic application and are available as rigid thermoplastic films, sheet, foams, and elastomers. Furthermore, styrene polymers form an important part of alloys/blends and thermoplastic elastomers (TPEs).

Styrene polymers comprise about 12% of total U.S. resin sales; 15% of thermoplastic sales; and have equivalent volumes with poly-propylene -- the fourth ranking resin behind polyethylene , polypropylene and PVC.

1.3 USES OF STYRENE

In Plastics:

Styrene monomer is used to make a variety of styrene plastics, from expandable foam to higher end engineering plastics. End uses of styrene include disposable food service products, cabinets for electronics, CD holders, paper coatings, boat hulls, and interior automotive components. In the construction industry it is used to produce tube products, tanks, lighting fixtures, insulation, and various corrosion resistant and rubber products.

In food packaging:

The performance and price factor of polystyrene makes it idle for using it as a packaging material. Packaging materials need to prevent food from spoiling as well as protect it from damage during transport, storage as well as through the process of sale, and all of this while maintaining the strictest hygiene. Here polystyrene meets all these demands hence making it a suitable material for packaging.

When it comes to selecting the best food service packaging products, many educational food service systems recognize that polystyrene packaging delivers! No other food service packaging material provides polystyrene's unique combination of performance, economic, and environmental benefits. Polystyrene food service packaging is extremely strong yet lightweight, provides excellent insulation, enhances food service sanitation and contributes to protecting public health. It is less expensive than many other food service packaging options, and has less environmental impact during its manufacture and transport than paperboard food service packaging

Appearance is also important, and transparent food packaging plays a part in purchasing decisions. Various blends with Styrolux allow tailored solutions to be produced for particular applications. These include films, trays and cups.

In Refrigeration:

Polystyrene's tailored properties and easy processing combined with its unbeatable cost-effectiveness make it an ideal material for use in refrigeration equipment.

Whether for superb high-gloss surfaces or for any of the wide variety of accessories inside the refrigerator, the properties of polystyrene are equal to the task. Matt or colored, transparent or opaque

In Home:

Styrenic plastics are used in a broad variety of kitchen appliances both as a primary material of construction as well as for component use. The inner linings of fridges and freezers are typically made of products such as ABS or HIPS (High Impact Polystyrene), where toughness, chemical resistance and stiffness are all required. Where transparency is a requirement, such as for the transparent compartments found within these appliances SAN can be used. For items such as microwaves, cookers and extraction units for cooking odors (kitchen range vent), styrenic plastics are more likely to be used just as components such as buttons and dials. In smaller articles such as mixers and blenders, the housing, the exterior components and the accessories can all make good use of the properties available from styrenic plastics.

Consumer Electronics:

The tasks of writing letters, drawing, painting, and relying on sturdy luggage for your travels also depend on styrenic plastics. So do listening to music, watching television, playing video tapes or filming your family: consumer electronics is a rapidly growing market with a wide array of end uses where the versatility of styrenic plastics can be fully exploited.

In Offices:

Most of the office furnishings and equipment you've inherited are made from styrenic plastics; materials that have become indispensable in our working environment. Whether for your wood-finished desktop, computer monitor, letter trays, or the coat hanger behind your door, the properties of styrenic plastics products are equal to the task.

In neutral shades or brightly colored, transparent or opaque, they are not simply pleasing to the eye or touch -- they have important qualities that go far beyond mere aesthetics. Polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) or styrene-acrylonitrile (SAN) are amongst the products that make computer casings and monitors strong and heat-resistant; staplers resilient enough to withstand repeated impacts; jewel boxes a cost-effective solution to protect valuable CD-ROMs; and your desktop scratch-resistant despite years of use. Styrenic plastics' tailored properties and easy processing, combined with their remarkable cost-effectiveness, make them an ideal material for the intensively used equipment present in our modern offices.

In Construction:

As the importance of energy conservation grows, the need for highly effective insulation materials also increases. Expanded (EPS) or extruded (XPS) polystyrene insulation provides the long-term energy efficiency now demanded by the construction industry. Heating and cooling account for 50-70% of the energy costs for the average home. The stable thermal performance of these insulation materials can result in significantly lower heating and cooling costs - savings that really add up over the life of the structure. And their design flexibility means that their benefits can be used in every part of a building - from foundation, to walls, to roof. In addition to reducing energy costs, reducing energy use helps conserve non-renewable fuel supplies. And using more energy efficient materials and products in our construction, to decrease the use of fuel and energy, translates into reduced air pollution.

As a life saver:

Bicycle helmets made from impact-absorbing polystyrene-based plastics and composites contributed to a 60% decline in the U.S. death rate from bicycle-related injuries among children 14 and under during the period 1979-97.

Ring life floaters and children's pool toys stay afloat because they are made from polystyrene foam plastic, which has a highly buoyant closed-cell structure. (Closed cell foams totally encase the air bubbles that make up the foam and don't allow water to penetrate into the structure.) Even entire floating docks are kept safely afloat with polystyrene foam.

But tough, polyester resins are also used to make lifeboats for Coast Guard rescue operations as well as pleasure boats and cruise ships. And police keep the peace on motorcycles of the water, patrolling on jet skis that are made from styrenic materials. Using personal watercraft really cuts down on the accidents and fatalities.

In Medicines:

Many vaccines must be maintained at low temperatures. Easy enough when you have a refrigerator or freezer handy, but a big challenge when your task is to transport a batch of vaccines to another continent in tropical climates. Thanks to a special expanded polystyrene package, vaccines are being transported safely from one country to another. For example, each shipping unit can hold 400 freeze-dried 3ml vaccines together with 4 kg (10 pounds) of dry ice. The thermal insulation properties of expanded polystyrene maintain the required temperature inside the sealed package for 72 hours.

In hospital settings, single use food service materials are the preferred option, and the sanitary qualities of polystyrene single serve containers are a primary benefit of polystyrene food packaging and service materials for hospital use

ABS (acrylonitrile-butadiene-styrene) resin is used for the housing of a state-of-the-art blood analyzer because of its proven performance in applications that require strength, durability and a high-gloss surface to help ensure cleanliness in hospital settings. The hand-held system provides clinicians with a portable, nearly instantaneous analyzer that requires just two drops of whole blood to provide a wide range of tests needed in medical diagnoses. Styrene-based boxes also help to save lives by protecting organs while they are being transported for donation.

In Transportation:

The convenience and safety you enjoy in driving your car - as well as the benefits of lorry (truck) transport, aircraft, and construction machinery - all depend on styrene.

Styrene-based plastic materials are not only used in the automotive industry for their easy processability or the reduction of the vehicle assembly time and costs they help achieve. The weight savings achieved through plastics use are impressive, which helps minimize environmental impact (among other things through fuel savings) and save resources like cutting fuel. Styrene is also used to give tires better road-hugging ability, especially on wet roads.

New Scientist magazine reports that chemists have taught single molecules of polystyrene an impressive new trick - how to snatch and store energy from light in the way that plants do. Researchers are working on a new breed of polystyrene-based battery. They say that because polystyrene derivatives are inexpensive, the batteries could be used to power anything from cars to cellular telephones. The project is to find simple materials that can mimic the complex chemistry of photosynthesis, which allows plants to store energy from sunlight in chemical bonds

In Computers:

Toughness, heat-, scratch-, impact-resistance, smart surface finish, creative design, cost-effectiveness; these aren't the only qualities of styrenic plastics. One of the world leaders in computer design and manufacture conducted a case study on the need to combine in their products top quality, ease of manufacture, and cost-effectiveness - but with environmental responsibility. Their decision, justified by reduced cost and increased recyclability, was to use an integral acrylonitrile-butadiene-styrene (ABS) top cover for their latest model. In making their decision, the manufacturer considered ABS' key environmental performance attributes, including energy conservation, ease of disassembly of materials and recyclability of components and materials.

A study comparing housings for electrical and electronic equipment demonstrated that the environmental costs in production and at the end of life for styrene-based housings were one tenth those of aluminum alternatives.

1.4 HEALTH AND SAFETY:

The safety of employees is obviously an important factor to consider when designing a production process that utilizes potentially dangerous substances. According to the US Department of Labor Occupational Safety and Health Administration the following substances present in the production of styrene are considered hazardous air contaminants: styrene, ethyl benzene, benzene, toluene, and propane. The chart below shows the limits placed on emissions of these substances.

Substance	TWA	Acceptable Ceiling Concentration	Maximum Peak Concentration
Styrene	50 ppm	100 ppm	200 ppm
Ethylbenzene	100ppm	125 ppm	
Benzene	1ppm	5ppm	
Toluene	200 ppm	300 ppm	500 ppm
Propane	1000 ppm		

(1) The TWA is the total weighted average over a typical eight-hour workday. The employee should not be exposed to an amount of the substance above the acceptable ceiling concentration at any time during the eight-hour shift. If a maximum peak concentration is given, exposure is allowed up to but not exceeding that concentration, but for no more than a set time limit (usually 10 minutes). Any exposure above the TWA concentration must be compensated for by exposure suitably below the TWA concentration.

Possible sources of these emissions are during transportation and storage of substances, equipment leaks and process vents

(2) Even with reliable equipment, anything is possible; therefore air quality should be regularly monitored to insure that contaminants remain at a safe level. Employees should be educated in the appropriate response should a spill or leakage occur.

Care should be taken in storage of flammable substances. Listed in order of increasing flash point these substances are: the hydrocarbon fuel mixture, benzene, toluene, ethylbenzene, and styrene. These substances are extremely flammable in both liquid and vapor state; therefore it is important that they be stored in a well ventilated area away from heat, ignition sources and open flame. Outside storage is recommended

(3). The above data is taken from the following soures:

(1) Data obtained from www.osha.gov

(2) Data obtained from www.epa.gov/ttnchiel/le/styrene.pdf

(3) Data obtained from http://siri.org/msds/gn.cgi

1.5 ENVIRONMENTAL CONCERNS:

The primary environmental concern associated with the production of styrene is the combustion of the hydrogen-hydrocarbon fuel mixture. Though the hydrocarbon fuel mixture is relatively clean burning when compared to other sources such as coal(which contributes to acid rain), it does produce large amounts of greenhouse gases when combusted. According to the Energy Information Administration, in the year 2000 twenty-two thousand metric tons of methane was emitted from the production of styrene in the United States alone making it the second highest source of methane emissions among chemical production processes. Even more abundant than the methane is impact from the release of carbon dioxide into the atmosphere. Carbon dioxide in the atmosphere has increased approximately 10% since 1958 largely due to the burning of fossil fuels (4). Though the emission of some amount of these gases is inevitable, there are steps that can be taken to reduce the environmental impact.

By making energy efficiency a focus in the design of the styrene production plant one can decrease the amount of fuel consumed. This results not only in the reduction of greenhouse gas emissions but also reduces the long-term cost of production. Another way to help compensate for the environmental damage due to carbon dioxide emissions is the implementation of carbon sinks. Plants and trees which consume carbon dioxide as a part of their metabolic cycle are examples of natural carbon sinks. By making an effort to plant trees and keep up the environmental areas in the community we can help reduce the effect of greenhouse gases until a permanent solution is found.

(4) Data obtained from http://www.wikipedia.org

CHAPTER 2
PROCESS DESCRIPTION

2.1 THE BASIC PROCESS DESCRIPTION

Styrene is the monomer used to make polystyrene , which has a multitude of uses , the most common of which are in the packing and insulated styrofoam beverages cups. Styrene is produced by the dehydrogenation of ethylbenzene. Ethylbenzene is formed by reacting ethylene and benzene, and most benzene is mabe by hydrodealkylaiton of toluene, which is obtained as a byproduct of gasoline manufacture. There is very little ethylbenzene sold commercially. Most ethylbenzene manugacturers convert it directly into styrene.

Styrene production reactions:

$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2$ (EQ . 1)

$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4$ (EQ . 2)

$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4$ (EQ . 3)

PROCESS DESCRIPTION:

The process flow diagram is shown in Fig 1.In the Classic process, EB is catalytically dehydrogenated to styrene in the presence of steam. The reaction is carried out at high temperature under vacuum. The EB (fresh and recycle) and primary steam are combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor system (1). An interheater reheats the process gas between stages. Reactor effluents are cooled to recover waste heat and condense the hydrocarbons and steam. Uncondensed offgas is compressed and is used as fuel. Condensed hydrocarbons (2) are sent to the distillation section. Process condensate (2) is stripped to remove dissolved aromatics. A fractionation train (3,4) separates high-purity styrene, unconverted EB, which is recycled, and the relatively minor reaction byproduct tar. Toluene is produced (5,6) as a minor byproduct, and benzene (6) is recycled to the alkylator

Typical SM-product purity ranges from 99.8% to 99.95%. The process provides high-product yield due to a unique combination of catalyst and operating conditions used in the reactors.

2.2 THE COMMERCIALLY AVAILABLE PROCESS:

Lummus/UOP Smart SMTM Process :(SMART PROCESS)

The SMART process is the same except between the dehydrogenation stages; oxygen is introduced to partially oxidize the hydrogen produced over a proprietary catalyst, to reheat the process gas and to remove the equilibrium constraint for the dehydrogenation reaction. The process achieves up to or greater than 80% EB conversion per pass.

FEEDSTOCK AND PRODUCT:

Feedstock:
Ethylbenzene 99.85 wt-% min
Xylene 50 ppm wt-% max
Diethylbenzene 8 ppm wt-% max
Styrene Product:
Styrene 99.85 wt-% min
Ethylbenzene 0.03 wt-% max

COMMERCIAL EXPERIENCE:

Since the introduction of the Lummus/UOP Smart SM process in 1995, Lummus and UOP have been awarded 5 projects with styrene capacities ranging from 84,000 to 427,000 MTA. Five commercial plants are in operation worldwide having a total styrene capacity of more than 1,300,000 MTA.

2.3 THE PROCESS FLOWDIAGRAM

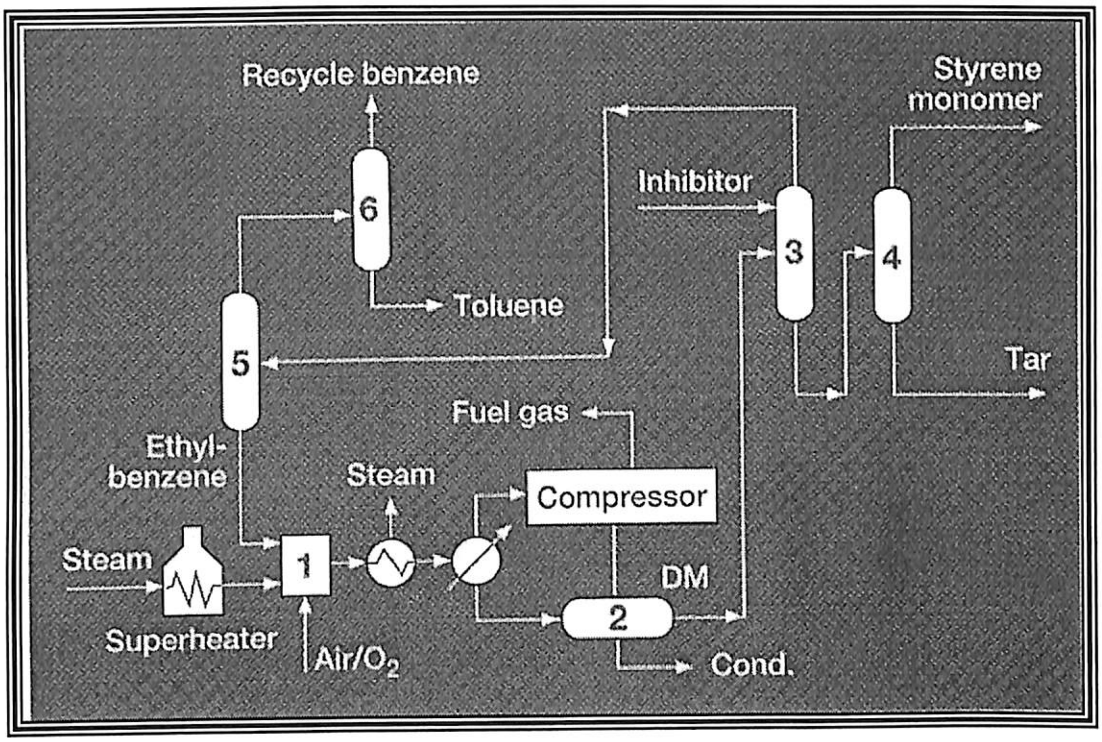


FIGURE 1

CHAPTER 3
DESIGN BASIS

3.1 THE KINETICS

The requested preliminary appraisal study should include all the process steps needed to manufacture 20 million pounds per year of styrene monomer from ethylbenzene.

Wenner and Dybdal (1) provided information on the reaction kinetics of the dehydrogenation of ethylbenzene. The following reactions were proposed as being important:

$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2$ (EQ . 1)

$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4$ (EQ . 2)

$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4$ (EQ . 3)

Equilibrium information indicates that reaction 1 is the only one with an important reverse reaction.

Reaction rate equations are given by Wenner and Dybdal (1) as follows (these pseudoelementary rate laws fit reaction kinetic data reasonably well):

$r_1 = k_1 (P_{EB} - P_{ST}P_{H2}/K_1)$ (Eq. 4)

$r_2 = k_2 P_{EB}$ (Eq. 5)

$r_3 = k_3P_{EB}P_{H2}$ (Eq. 6)

Effect of temperature on the reaction rate constants was interpreted from the experimental results as follows

$\log10k_1 = (-11{,}370/4.575\bullet T^{\circ}K) + 0.883$ (Eq. 7)

$\log10k_2 = (-50{,}800/4.575\bullet T^{\circ}K) + 9.13$ (Eq. 8)

$\log10k_3 = (-21{,}800/4.575\bullet T^{\circ}K) + 2.78$ (Eq. 9)

Reported experimental results were obtained with a packed-tube reactor, 0.75 in. i.d., 1.00 in. o.d. by 78 inches overall length. A preheat section of 1.5 ft. was packed with 6-mm porcelain Berl saddles followed by a 4-foot long catalyst section containing 348 cc of catalyst. Temperature was measured by a thermocouple in the catalyst bed 12 in. from the exit. Results of detailed calculations show that the effect of diffusion in the pores of the catalyst pellets was probably a significant factor in the rate mechanisms. However, given the same similitude of catalyst pellet size and pore structure, a reasonably accurate rate replication and scale-up can be obtained. Catalyst regeneration in the present project can be accomplished with a periodic superheated-steam treatment.

A shell-and-tube heat-exchanger-type packed tube reactor should be used to provide the necessary large heat transfer area per unit catalyst volume. Ethylbenzene along with steam can be fed into the tubes filled with platinum catalyst on a silica-alumina carrier. Steam acts as an inert shifting the equilibrium of reaction 1 to the right, while hot flue gas can be passed countercurrently on the shell-side. Since, we do not have information on the hot flue gas we will not consider it and assume the reactor to be adiabatic. Reactor design variables are too numerous unless some variables are fixed at reasonable or typical values. Variables include: tube length and diameter, catalyst shape and size, feed temperature, heating medium temperature, mass velocity of the feed stream and others. Tables I contains lists of tentative fixed parameters and variables in this study. The experimental results of Wenner and Dybdal provide the basis and bench-mark values for those listed in the following tables.

Assume that the pressure drop is given by the Ergun equation, (BSL-Eq. 6.4-14, p. 200 or p 696 Peters and Timmerhaus, or p 177 Folger).

3.2 TABLE I: FIXED PARAMETERS AND VARIABLES FOR REACTOR DESIGN

Catalyst: alumina, 1/8-inch spheres, $\rho_C = 61$ lb/ft^3, $\rho_P = 117$ lb/ft^3
d_i, d_o = 4.03 in., 4.50 in.
$\Phi = 0.48$, d_c = 1/8 in., $\rho_p = 117.3$ lb/ft^3 catalyst
F_0 = 4 lb-moles/h-tube
P_0 = 1.382 atm , T_0 = 1292°F,
Purchase cost = $4.20/lb (12/84)
Reactor tubes and tube-sheet: 316 stainless steel -------- contd

Length of the tube = 20 ft.

Superficial mass velocity of reactor feed: 3600 $lb_m/hr \times ft^2$

Based on the styrene design project, our objective is to do the following:

Derive the equations we would use to find the following quantities as a function of axial position in the reactor:

Molarflowrates of all species in lbmol/hr

Temperature of the reaction mixture: T(°F)

Pressure of the reaction mixture (atm)

Express your equations in terms of the parameters given in the design project description:

Assume the viscosity of the reaction mixture to be 0.02 cp, where 1 cp = 6.72×10^{-4} lbm/ft×s.

Assume the pressure drop is given by the Ergun equation.

Make it clear how you will determine X(z), Y(z), and T(z) from the dependent variables of your design equations. Then sketch the expected shapes of F_E, F_S, F_H, X, Y, XY, and T vs. z.

Calculate the number of tubes and their length required to produce 2.0×10^7 lb. styrene per year with a fractional conversion of ethylbenzene of roughly 30%.

For your information, I am summarizing below the results of studies performed by Wenner and Dybdal [*Chem. Eng. Progr.*, **44**, 275 (1948)] and Bodman [The Industrial Practice of Chemical Process Engineering, MIT Press (1968)] on this reaction system, along with thermochemical data you will need.

3.3 THERMOCHEMICAL AND KINETIC DATA FOR ETHYLBENZENE-STYRENE SYSTEM (EQUATIONS OF BODMAN CORRECTED FOR MASS TRANSFER RESISTANCE IN THE CATALYST PARTICLE)

$\log10k_1 = (-11{,}370/4.575 \cdot T^{\circ}K) + 0.883$

$\log10k_2 = -50\,800/(4.575 \cdot T^{\circ}K) + 9.13$

$\log10k_3 = -21\,800/(4.575 \cdot T^{\circ}K) + 2.78$

T in Kelvin,

k in lb-mole/(hr•lb catalyst•atm) or lb-mole/(hr•lb catalyst•atm^2)

$K_1 = 2.8 \times 10^{-2}$ atm

Substance .	H_{of} @ 77°F, BTU/lb-mole	Cp[T(°F)], vapor-phase heat capacities BTU/(lb-mole °F)
Ethylbenzene (g)	+12,816	$26.18 + 0.0602T - 1.84 \times 10^{-5}T^2$
Styrene (g)	+63,396	$25.12 + 0.0542T - 1.71 \times 10^{-5}T^2$
Hydrogen (g)	0	$6.89 + 3.94 \times 10\text{-}5T + 2.11 \times 10^{-7}T^2$
Benzene (g)	+35,676	$16.29 + 0.043lT - 1.37 \times 10^{-5}T^2$
Ethylene (g)	+22,491	$9.25 + 0.0155T - 5.08 \times 10^{-6}T^2$
Toluene (g)	+21,510	$20.86 + 0.0523T - 1.58 \times 10^{-5}T^2$
Methane (g)	-32,202	$7.94 + 7.66 \times 10\text{-}3T - 3.60 \times 10^{-7}T^2$
Steam (g)	-	$(3.470 + 1.450 \times T) \times 0.2388$

Data taken from http:// cheweb.tamu.edu

CHAPTER 4
SOLUTION PROCEDURE

In reaction systems consisting of many parallel and consecutive reactions, it may not be possible to solve the reaction problem using fractional conversion. An alternative approach is to carry out mole balances on each species and write the resulting equations as a function of the number of moles of each species N_j in a batch system or as a function of the molar flowrates F_j in a flow system. The energy balance and momentum balance are also written for the whole system. The resulting coupled differential equations are then solved either with a numerical package or by writing an ODE solver. The design problem in this project is solved using an ODE solver called POLYMATH.

4.1 THE MOLE BALANCES:

The generic sequence of q reactions is shown below:

Reaction number	Reaction stoichiometry
1	$v_{11}A_1 + v_{12}A_2 \rightarrow v_{1j}A_J$
2	$v_{21}A_1 + v_{2j}A_j \rightarrow v_{23}A_3 + v_{24}A_4$
i	$v_{ij}A_j + v_{ik}A_k \rightarrow v_{ip}A_p$
q	$v_{qj}A_j + v_{q3}A_3 \rightarrow v_{q5}A_5$

The first subscript in the stochiometric coefficient, v_{ij} (and in the reaction rate r_{ij}) refers to the reaction number and the second to the particular species in the reaction.

In analyzing the multiple reactions in the Table above, we carry out the following (not necessarily the following order):

1. Basis of calculation. Divide the reaction through by the stoichiometric coefficient for which the rate law is given.
2. Determine the rate laws for each species in each reaction.
3. Determine the net rate of disappearance or formation of each chemical species
4. Express rate laws as a function of concentration, C_j, for the case of no volume change. When there is volume change with reaction, express the rate laws as a function of moles, N_j (Batch), or molar flow rates, Fj (Flow).
5. Write the mole balances.

Wenner and Dybdal (1) provided information on the kinetics of the dehydrogenation of ethylbenzene.The following reactions were proposed as being important:

$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2$ (EQ 1)
(EB) (ST) (H2)
$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4$ (EQ 2)
(EB) (B) (ET)
$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4$ (EQ 3)
(EB) (H2) (T) (M)

Reaction rate equations are given by Wenner and Dybdal (1) as follows (these pseudo elementary rate laws fit reaction kinetic data reasonably well):

$r_{1ST} = k_1(P_{EB} - P_SP_{H2}/K_1)$
$r_{2B} = k_2P_{EB}$
$r_{3T} = k_3P_EP_{H2}$

Effect of temperature on the reaction rate constants was interpreted from the experimental results as follows:

$Log_{10}k_1 = (-11370/4.575\times T^0K) + 0.883$
$Log_{10}k_2 = (-50800/4.575\times T^0K) + 9.33$

$Log_{10}k_3 = (-21800/4.575 \times T^0K) + 2.78$

Stoichiometry:

$r_{1ST} = r_{1H2} = -r_{1EB}$

$r_{2B} = r_{2E} = -r_{2EB}$

$r_{3T} = r_{2M} = - r_{3EB} = -r_{3H2}$

Net Rates Of Formation:

Species EB (ethylbenzene) : $r_{EB} = r_{1EB} + r_{2EB} + r_{3EB}$

$= - r_{1ST} - r_{2B} - r_{3T}$

Species ST (styrene) : $r_{ST} = r_{1ST} + r_{2ST} + r_{3ST}$

$= r_{1ST}$

Species H2 (hydrogen) : $r_{H2} = r_{1H2} + r_{2H2} + r_{3H2}$

$= r_{1ST} - r_{3T}$

Species B (benzene) : $r_B = r_{1B} + r_{2B} + r_{3B}$

$= r_{2B}$

Species ET (ethylene) : $r_{ET} = r_{1ET} + r_{2ET} + r_{3ET}$

$= r_{2B}$

Species T (toluene) : $r_T = r_{1T} + r_{2T} + r_{3T}$

$= r_{3T}$

Species M (methane) : $r_M = r_{1M} + r_{2M} + r_{3M}$

$= r_{3T}$

The general form of mole balance for a species is

Rate of flow of species j into the system	+	Rate of flow of generation of species j by reaction	-	Rate of flow of species j out of the system	=	Rate of accumulation of species j within the system

$$F_{j0} \quad + \quad G_j \quad - \quad F_j \quad = \quad dN_j/dt$$

$G_j = r_j.V$

Where, r_j = net formation of species j in multiple reaction system.

V = reaction volume

The equation when applied to tubular rector becomes

$$F_{j0} - F_j + \int r_j dV = dN_j/dt$$

At steady state the mole balance becomes

$$F_{j0} - F_j + \int r_j dV = 0$$

Over a differential volume where spatial variation of r_j is neglected , the mole balance becomes

$$dF_j/dv = r_j$$

We now write the mole balances:

Species EB : $dF_{EB}/dV = r_{EB} = r_{1ST} - r_{2EB} - r_{3T}$

Species ST : $dF_{ST}/dV = r_{ST} = r_{1ST}$

Species H2 : $dF_{H2}/dV = r_{ST} = r_{ST} - r_{3T}$

Species B : $dF_B/dV = r_B = r_{2B}$

Species ET : $dF_{ET}/dV = r_B = r_{2B}$

Species T : $dF_T/dV = r_T = r_{3T}$

Species M : $dF_M/dV = r_M = r_{3T}$

Total $F_T = F_{EB} + F_{ST} + F_{H2} + F_B + F_{ET} + F_T + F_M + F_{I0}$

Where , F_T = Total molarflowarte of the gas in lbmol/hr

F_{EB} = Molarflowrate of ethylbenzene in lbmol/hr

F_{ST} = Molarflowrate of styrene in lbmol/hr

F_{H2} = Molarflowrate of hydrogen in lbmol/hr

F_B = Molarflowrate of benzene in lbmol/hr

F_{ET} = Molarflowrate of ethylene in lbmol/hr

F_T = Molarflowrate of toluene in lbmol/hr

F_M = Molarflowrate of methane in lbmol/hr

F_{I0} = Molarflowrate of steam in lbmol/hr

$r_{1ST} = k_1(P_{EB} - P_S P_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2 P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3 P_E P_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

4.2 ENERGY BALANCE :

First Law of Thermodynamics:

For a closed system, in which no mass crosses the system boundaries, the change in total energy, dE, of the system is equal to the heat flow, dQ, to the system minus the work, dW, done by the system on the surroundings for the closed system the energy balance is

$dE = dQ - dW$

For the continuous flow reactors which are open systems in which mass crosses the system boundary. The energy balance for only one species entering becomes

Rate of Accumulation of energy within the system of energy	=	Rate of flow of heat to the the system from the surrounding	-	Rate of work done by the system on the surrounding	+	Rate of energy flow flow into the system by mass	-	Rate of energy flow out of the the system by mass

$$dE/dt \quad = \quad Q^{\cdot} \quad - \quad W \quad + \quad F_{in}E_{in} \quad - \quad F_{out}E_{out}$$

$$(dE/dt)_{sys} = Q^{\cdot} - W + \Big(\sum_{j=1}^{m} E_jF_j\Big)_{in} - \Big(\sum_{j=1}^{m} F_iE_j\Big)_{out}$$

Evaluating the work term:

It is customary to separate the work term, $W^{\cdot}$, into flow work and other work , $W^{\cdot}_s$. Flow work is work that is necessary to get the mass into and out of the system.

$$W^{\cdot} = \sum_{j=1}^{m} F_jPV_i\Big|_{in} - \sum_{j=1}^{m} F_jPV_j\Big|_{out} + W^{\cdot}_s$$

where P is the pressure and V_j the specific volume.

The term $W^{\cdot}_S$ is often referred to as the shaft work, and could be produced from such things as a stirrer in a CSTR or a turbine in a PFR. In most instances, the flow work is combined with these terms in the energy balance that represent the energy exchange by mass flow across the system boundaries. Substituting the work term in the energy balance gives

$$(dE/dt)_{sys} = Q^{\cdot} - W_s + \sum_{j=1}^{m} F_j(E_j + PV_j)_{in} - \sum_{j=1}^{m} F_j(E_j + PV_j)_{out}$$

The energy E_j is the sum of the internal energy (U_j), the kinetic energy ($u^2_j/2$), the potential energy (gz_j) and any other energies, such as electric or magnetic energy or light:

$E_j = U_j + u^2_j/2 + gz_j + \text{other}$

In almost all chemical reactor situations, the kinetic, potential and other energy terms are negligible in comparison with the enthalpy, heat transfer and work terms and hence will be omitted; i.e.,

$E_j = U_j$

We recall that enthalpy, H_j, is defined in terms of internal energy U_j and the product PV_j

$H_j = U_j + PV_j$

Substituting for H_j in the energy balance we get:

$$(dE/dt)_{sys} = Q^{\cdot} - W_s + \sum_{j=1}^{m} (F_jH_j)_{in} - \sum_{j=1}^{m} (F_jH_j)_{out}$$

We shall let the subscript "0 "represent inlet conditions. Unsubscripted variable represent the conditions at the outlet of the chosen system volume.

$$(dE/dt)_{sys} = Q^{\cdot} - W_s + \sum_{j=1}^{m} F_{j0}H_{j0} - \sum_{j=1}^{m} F_jH_j$$

At steady state the energy balance becomes

$$Q^{\cdot} - W_s + \sum_{j=1}^{m} F_{j0}H_{j0} - \sum_{j=1}^{m} F_jH_j = 0$$

Normally in systems involving chemical reactions the shaft work is negligible compared to other forms of energy and hence neglected, the energy balance now becomes

$$Q^{\cdot} + \sum_{j=1}^{m} F_{j0}H_{j0} - \sum_{j=1}^{m} F_jH_j = 0$$

Evaluating the heat transfer term , Q. :

The heat transfer across the system boundary is given by

$$Q^{\cdot} = UaV(T_{fg} - T)$$

Where,

U = Overall heat transfer coefficient BTU/hr.ft^2.^{0}F

a = Heat transfer area per unit volume ft^{-1}

T_{fg} = Temperature of the flue gases in ^{0}F

We plan to reduce the energy balance to more useful form for a plug flow reactor. We begin by applying the energy balance to a small differential volume , ΔV, in which there are no spatial variations.

$$\Delta Q^{\cdot}/\Delta V + (\sum_{j=1}^{m} F_{j0}H_{j0} \big|_{V+\Delta V} - \sum_{j=1}^{m} F_jH_j \big|_{V})/\Delta V = 0$$

Taking the limit as $\Delta V \rightarrow 0$ gives

$$dQ^{\cdot}/dV - d\sum_{j=1}^{m} F_jH_j /dV = 0$$

$$dQ^{\cdot}/dV - \sum_{j=1}^{m} F_jdH_j /dV - \sum_{j=1}^{m} H_idF_i / dV = 0$$

We know that $dH_j = C_{pj}dT$

For plug flow reactor $dFj / dV = r_j$

The rate of reaction of species j is related to the rate of disappearance of known species A through the stoichiometric coefficient v_j

$r_j = v_j(-r_A)$

Substituting for $Q^{\cdot}$, dH_j , dF_j / dV in the energy balance gives

$$Ua(T_{fg} - T) - \sum_{j=1}^{m} F_j C_{pj} dT/dV + (-r_A)(-\sum v_j H_j) = 0$$

$$Ua(T_{fg} - T) - \sum_{j=1}^{m} F_j C_{pj} dT/dV + (-r_A)(-\Delta H_R(T)) = 0$$

In case of multiple reaction the energy balance becomes

$$Ua(T_{fg} - T) - \sum_{j=1}^{m} F_j C_{pj} dT/dV + \sum_{i=1}^{q} (-r_{ij})(-\Delta H_{Rij}(T) = 0$$

Rearranging the energy balance gives

$$dT/dV = \sum_{i=1}^{q} (-r_{ij})(-\Delta H_{Rij}(T)) / \sum_{j=1}^{m} F_j C_{pj}$$

$$\Delta H_{Rij}(T) = \Delta H_{Rij}(T_R) + \int_{TR}^{T} Cp_j dT$$

Where,

T = Temperature of gas in ^{0}F

r_{ij} = rate of formation of jth species in the ith reaction in lbmol/hr.lbcat

$\Delta H_{Rij}(T)$ = Heat of reaction at temperature T in BTU/lbmol

F_j = Molar flowrate of jth species in lbmol/hr

Cp_j = Molar specific heat of the jth species in BTU/lbmol.^{0}F

$\Delta H_{Rij}(T_R)$ = Heat of reaction i with respect to jth species at the refermce temperature in BTU/lbmol.

For an adiabatic reactor the energy balance becomes:

$$dT/dV = \sum_{i=1}^{q} (-r_{ij})(-\Delta H_{Rij}(T)) / \sum_{j=1}^{m} F_j C_{pj}$$

4.3 THE MOMENTUM BALANCE:

The majority of gas phase reactions are catalyzed by passing the reactants through a packed bed of catalyst particles. The equation used most to calculate pressure drop in a packed porous bed is the **Ergun equation.**

$$dP/dL = - G/\rho g_c D_p\{(1 - \Phi)/\Phi^3\}[\ 150(1-\Phi)\mu/D_p\ +\ 1.7G\ ]$$

where

P = pressure , lb/ft^2

Φ = porosity = volume of void/total bed volume

$1- \Phi$ = volume of solid/total bed volume

$g_c = 32.174\ lb_m.ft/s^2.lb_f = 4.17 \times 10^8\ lb_m.ft/s^2.lb_f$

D_p = diameter of paticle in the bed, ft

μ = viscosity of gas passing through the bed, $lb_m/ft.hr$

L = length down the tube, ft

u = superficial velocity= volumetric flow/cross sectional area of tube, ft/hr

ρ = gas density, lb/ft^3

$G = \rho u$ = superficial mass velocity, $g/cm^2.s$ or $lb_m/ft^2.hr$

The mole balances , the energy balance and the momentum balance are solved simultaneously to get the molarflowrates, temperature and pressure at the end of the reactor length.

CHAPTER 5
CALCULATIONS

5.1 THE MOLE BALANCES:

We express the mole balances in terms of length of the tube:

The cross-sectional area of the tube = 0.0885 ft^2

The density of catalyst particle = 117 lb/ft^3

The rate laws given in lbmol/hr.lbcat are converted into lbmol/hr.ft of length of the tube

Species EB : $dF_{EB}/dL = r_{EB} = (r_{1ST} - r_{2EB} - r_{3T}) \times \rho_p \times A$
$= (r_{1ST} - r_{2EB} - r_{3T}) \times 117 \times 0.0885$

Species ST : $dF_{ST}/dL = r_{ST} = r_{1ST} \times \rho_p \times A$
$= r_{1ST} \times 117 \times 0.0885$

Species H2 : $dF_{H2}/dL = r_{ST} = (r_{ST} - r_{3T}) \times \rho_p \times A$
$= (r_{ST} - r_{3T}) \times 117 \times 0.0885$

Species B : $dF_B/dL = r_B = r_{2B} \times \rho_p \times A$
$= r_{2B} \times 117 \times 0.0885$

Species ET : $dF_{ET}/dL = r_B = r_{2B} \times \rho_p \times A$
$= r_{2B} \times 117 \times 0.0885$

Species T : $dF_T/dL = r_T = r_{3T} \times A$
$= r_{3T} \times 0.0885$

Species M : $dF_M/dL = r_M = r_{3T} \times \rho_p \times A$
$= r_{3T} \times 117 \times 0.0885$

Total $F_T = F_{EB} + F_{ST} + F_{H2} + F_B + F_{ET} + F_T + F_M + F_{I0}$

Where ,

$r_{1ST} = k_1(P_{EB} - P_S P_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2 P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3 P_E P_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

$\log 10 k_1 = (-11{,}370/4.575 \cdot T^oK) + 0.883$ (Eq. 7)

$\log 10 k_2 = (-50{,}800/4.575 \cdot T^oK) + 9.13$ (Eq. 8)

$\log 10 k_3 = (-21{,}800/4.575 \cdot T^oK) + 2.78$ (Eq. 9)

Since the energy balance gives temperature in ^0F , it has to be converted into ^0K so as to substitute in Eq's 7 , 8 and 9

After substitution the Eq's 7 , 8 and 9 become

$\log_{10}k_1 = (-11370/4.575\times(T + 459.67)/1.8\ ^0K) + 0.883$

$\log_{10}k_2 = (-50800/4.575\times(T + 459.67)/1.8\ ^0K) + 9.13$

$\log_{10}k_3 = (-21800/4.575\times(T + 459.67)/1.8\ ^0K) + 2.78$

K_1 = Equilibrium constant = 0.028 atm

T = Temperature of the gas in ^0F

In order to solve the mole balances the rate laws have to be expressed in terms of concentrations and then in terms of molarflowrates along the length of the tube.

We can do this using the ideal gas law:

$P_{ST} = C_{ST}\times R\times(T + 459.67)$

C_{ST} = Concentration of styrene in the gas , lbmol/ft^3

R = Universal gas constant = 0.73 ft^3.atm/lbmol.^{0}R

T = Temperature of the gas in ^0F

Concentration of styrene in terms of its flowrate can be expressed using the ideal gas law

$PV = ZN_TRT$

Where, P = Total pressure of the gas in atm

V = Total volume of the gas in ft^3

Z = Compressibility factor = 1

R = Universal constant = 0.73 ft^3.atm/lbmol.^{0}R

T = temperature of the gas ^0F

N_T = Total number of moles of styrene

The ideal gas equation is valid at any point in the system at any time t. At initial conditions

$P_0V_0 = Z_0N_{T0}RT_0$

$Z_0 = Z = 1$ (assume)

Dividing PV by P_0V_0 gives

$V = V_0(P_0/P)(T/T_0)(N_T/N_{T0})$

In case of flow systems N_T and N_{T0} are replaced by F_T and F_{T0} respectively

Hence, $V = V_0(P_0/P)(T/T_0)(F_T/F_{ST0})$

The concentration of styrene is given by

$C_{ST} = F_{ST}/V$

Substituting for V gives

$C_{ST} = F_{T0}/V_0 \times F_{ST}/F_T \times T_0/(T + 459.67) \times P/P_0$

$C_{ST} = C_{T0} \times F_{ST}/F_T \times T_0/(T + 459.67) \times P/P_0$ (since $C_{T0} = F_{T0}/V_0$)

Where ,

T = Temperature of the gas in ^{0}F

P = Pressure of the gas in atm

T_0 = Initial temperature of the gas in ^{0}R = 1751.67 ^{0}R

P_0 = Initial pressure of the gas in atm = 1.382 atm

C_{T0} = Initial concentration of the gas in lbmol/ft^3

= $P_0 \times R \times T_0$

= 0.00108 lbmol/ft^3

5.2 THE ENERGY BALANCE

The relation between temperature and length of the tube is given by the energy balance

$$dT/dV = \sum_{i=1}^{q} (-r_{ij} \times \rho_p)(-\Delta H_{Rij}(T)\ )/ \sum_{j=1}^{m} F_j\, C_{pj}$$

$$dT/dL = \sum_{i=1}^{q} (-r_{ij} \times \rho_p \times A)(-\Delta H_{Rij}(T)\ \}/ \sum_{j=1}^{m} F_j\, C_{pj}]$$

$dT/dL = ((r_{1ST} \times (-\text{delta}H_{r1EB}) + r_{2B} \times (-\text{delta}H_{rEB}) + r_{3T} \times (-\text{delta}H_{r3EB}))/(F_{EB} \times C_{PEB} + F_{ST} \times C_{PST} + F_{H2} \times C_{PH2} + F_B \times C_{PB} + F_{ET} \times C_{PET} + F_T \times C_{PT} + F_M \times C_{PM} + F_{I0} \times C_{PI0})) \times 117 \times 0.0885\ {}^0F/ft$

Where, $r_{1ST} = k_1(P_{EB} - P_S P_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2 P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3 P_E P_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

$Log_{10}k_1 = (-11370/4.575 \times (T + 459.67)/1.8\ {}^0K) + 0.883$

$Log_{10}k_2 = (-50800/4.575 \times (T + 459.67)/1.8\ {}^0K) + 9.13$

$Log_{10}k_3 = (-21800/4.575 \times (T + 459.67)/1.8\ {}^0K) + 2.78$

Substance .	H_{of} @ 77°F, BTU/lb-mole	Cp[T(°F)], vapor-phase heat capacities BTU/(lb-mole °F)
Ethylbenzene (g)	+12,816	$26.18 + 0.0602T - 1.84 \times 10^{-5}T^2$
Styrene (g)	+63,396	$25.12 + 0.0542T - 1.71 \times 10^{-5}T^2$
Hydrogen (g)	0	$6.89 + 3.94 \times 10^{-5}T + 2.11 \times 10^{-7}T^2$
Benzene (g)	+35,676	$16.29 + 0.043IT - 1.37 \times 10^{-5}T^2$
Ethylene (g)	+22,491	$9.25 + 0.0155T - 5.08 \times 10^{-6}T^2$

Toluene (g)	+21,510	$20.86 + 0.0523T - 1.58 \times 10^{-5}T^2$
Methane (g)	-32,202	$7.94 + 7.66 \times 10^{-3}T - 3.60 \times 10^{-7}T^2$
Steam (g)	-	$(3.470 + 1.450\times T)\times 0.2388$

Where , A = Cross-sectional area of the tube = 0.0855 ft^2

T = Temperature of gas in ^0F

r_{ij} = rate of formation of j^{th} species in the i^{th} reaction in lbmol/hr.lbcat

$\Delta H_{Rij}(T)$ = Heat of reaction at temperature T in BTU/lbmol

F_j = Molar flowrate of j^{th} species lbmol/hr

Cp_j = Molar specific heat of the j^{th} species BTU/lbmol.^0F

5.3 THE MOMENTUM BALANCE

The relation between pressure and the length of the reactor is given by the momentum balance

$dP/dL = - G/\rho g_c D_p\{(1 - \Phi)/\Phi^3\}[\, 150(1-\Phi)\mu/D_p + 1.7G\,]$

where

P = pressure , lb/ft^2

Φ = porosity = volume of void/total bed volume = 0.48

1- Φ = volume of solid/total bed volume = 0.52

$g_c = 32.174\ lb_m.ft/s^2.lb_f = 4.17 \times 10^8\ lb_m.ft/hr^2.lb_f$

D_p = diameter of paticle in the bed, ft = 1.8 in

μ = viscosity of gas passing through the bed, $lb_m/ft.h$ = 6.72 $lb_m/ft.sec$

L = length down the tube, ft =20 ft

ρ = gas density, lb_m/ft^3 = 0.413 lb_m/ft^3

G = ρu = superficial mass velocity, $g/cm^2.s$ or $lb_m/ft^2.hr$ = 3600 $lb_m/ft^2.hr$

Substituting the values in the momentum balance gives

dP/dL = -0.02 atm/ft

An ODE solver is used to solve the mole balances , the energy balance and the momentum balance .The polymath program is given in the next section.

5.4 THE POLYMATH PROGRAM FOR A SINGLE TUBE IN A PACKED TUBE REACTOR IS GIVEN BELOW:

$dF_{EB}/dL = (-r_{1ST} - r_{2B} - r_{3T})\times117\times0.0885$; Change in molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$F_{EB}(0) = 4.0$, Initial molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$dF_{ST}/dL = r_{1ST}\times117\times0.0885$; Change in molarflowrate of styrene in the gas in lbmol/hr.ft

$F_{ST}(0) = 0$, Initial molarflowrate of styrene in the gas in lbmol/hr.ft

$dF_{H2}/dL = (r_{1ST} - r_{3T})\times117\times0.0885$; Change in molarflowrate of hydrogen in the gas in lbmol/hr.ft

$F_{H2}(0) = 0$, Initial molarflowrate of hydrogen in the gas in lbmol/hr.ft

$dF_{B}/dL = r_{2B}\times117\times0.0885$; Change in molarflowrate of benzene in the gas in lbmol/hr.ft

$F_{B}(0) = 0$, Initial molarflowrate of benzene in the gas in lbmol/hr.ft

$dF_{ET}/dL = r_{2B}\times117\times0.0885$; Change in molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$F_{ET}(0) = 0$, Initial molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$dF_{T}/dL = r_{3T}\times117\times0.0885$; Change in molarflowrate of toluene in the gas in lbmol/hr.ft

$F_{T}(0) = 0$, Initial molarflowrate of toluene in the gas in lbmol/hr.ft

$dF_{M}/dL = r_{3T}\times117\times0.0885$; Change in molarflowrate of methane in the gas in lbmol/hr.ft

$F_{M}(0) = 0$, Initial molarflowrate of methane in the gas in lbmol/hr.ft

$r_{1ST} = k_1(P_{EB} - P_S P_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2 P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3 P_E P_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

$\mathrm{Log}_{10}k_1 = (-11370/4.575\times(T + 459.67)/1.8\ {}^{0}K) + 0.883$

$\mathrm{Log}_{10}k_2 = (-50800/4.575\times(T + 459.67)/1.8\ {}^{0}K) + 9.13$

$\mathrm{Log}_{10}k_3 = (-21800/4.575\times(T + 459.67)/1.8\ {}^{0}K) + 2.78$

$P_{EB} = C_{EB}\times R\times(T + 459.67)$, Partial pressure of ethylbenzene in the gas in atm

$P_{ST} = C_{ST}\times R\times(T + 459.67)$, Partial pressure of styrene in the gas in atm

$P_{T} = C_{T}\times R\times(T + 459.67)$, Partial pressure of toluene in the gas in atm

$C_{EB} = C_{T0}\times F_{EB}/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of ethylbenzene along the length of the tube in $lbmol/ft^3$

$C_{ST} = C_{T0}\times F_{ST}/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of styrene along the length of the tube in $lbmol/ft^3$

$C_T = C_{T0}\times F_T/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of toluene along the length of the tube in $lbmol/ft^3$

$K_1 = 0.028$, Equilibrium constant for reaction 1 in atm

$C_{T0} = 0.00108$, Initial concentration of the gas in $lbmol/ft^3$

$R = 0.73$, Universal gas constant in $ft^3\times atm/lbmol.^0R$

$F_T = F_{EB} + F_{ST} + F_{H2} + F_{ET} + F_T + F_M + F_{I0}$, Total molarflowrate of the gas in lbmol/hr

$F_{I0} = 4\times$Molarflowrate of ethylbenzene in lbmol/hr = 16 lbmol/hr

$T_0 = 1751.67^0R$, Initial temperature of the gas in ^0R

$P_0 = 1.382$, Initial pressure of the gas in atm

T= Temperature of the gas in ^0F

P = Pressure of the gas in atm.

$dT/dL = (r_{1ST}\times(-deltaH_{r1EB}) + r_{2B}\times(-deltaH_{rEB}) + r_{3T}\times(-deltaH_{r3EB})/(F_{EB}\times C_{PEB} + F_{ST}\times C_{PST} + F_{H2}\times C_{PH2} + F_B\times C_{PB} + F_{ET}\times C_{PET} + F_T\times C_{PT} + F_M\times C_{PM} + F_{I0}\times C_{PI0})\times 117\times 0.0885$ Temperature drop across the length of the tube in $^0F/ft$

$T_0 = 1292\ ^0F$, Initial temperature of the gas

$deltaH_{r1EB} = 50580 + 5.83\times(T-T_R) - 0.00596/2\times(T^2 - T_R^2) + 0.151\times(10^{-5}/3)\times(T^3 - T_R^3)$, Heat of reaction 1 with respect to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r2EB} = 45351 - 0.64\times(T-T_R) - 0.0034/2\times(T^2 - T_R^2) -0.461\times(10^{-5}/3)\times(T^3 - T_R^3)$, Heat of reaction 2 with respect to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r3EB} = -23508 + 2.62\times(T-T_R) - 0.00024/2\times(T^2 - T_R^2) - 0.3\times(10^{-7}/3)\times(T^3 - T_R^3)$, Heat of reaction 3 with respect to ethylbenzene in BTU/lbmolethylbenzene

$T_R = 77^0F$

$C_{PST} = 25.12 + 0.0542\times T - 1.71\times 10^{-5}\times T^2$, Heat capacity of styrene in $BTU/lbmol.^0F$

C_{PEB}= $26.18 + 0.0602\times T - 1.84\times10^{-5}\times T^2$,Heat capacity of ethylbenzene in BTU/lbmol^{0}F

C_{PH2}= $6.89 + 3.94\times10^{-5}\times T + 2.11\times10^{-7}\times T^2$,Heat capacity of hydrogen in BTU/lbmol.^{0}F

$C_{PB} = 16.29 + 0.0431\times T - 1.37\times10^{-5}\times T^2$, Heat capacity of benzene in BTU/lbmol.^{0}F

$C_{PET} = 9.25 + 0.0155\times T - 5.08\times10^{-6}\times T^2$, Heat capacity of ethylene in BTU/lbmol.^{0}F

$C_{PT} = 20.86 + 0.0523\times T - 1.58\times10^{-5}\times T^2$, Heat capacity of toluene in BTU/lbmol.^{0}F

$C_{PM} = 7.94 + 0.0602\times T - 1.84\times10^{-5}\times T^2$, Heat capacity of methane in BTU/lbmol.^{0}F

$C_{PI0} = (3.470 + 1.450\times T)\times0.2388$, Heat capacity of steam in BTU/lbmol.^{0}F

dP/dL = -0.02 , Pressure drop across the length of the tube in atm/ft

P(0) = 1.382 atm

L(0) = 0

L(f) = 20 ft

5.5 THE POLYMATH SOLUTION REPORT FOR A TUBE IN A PACKED TUBE REACTOR IS GIVEN IN THE NEXT PAGE

POLYMATH Report
Ordinary Differential Equations

No Title
13-May-2006

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	L	0	0	20.	20.
2	Feb	4.	3.025915	4.	3.025915
3	Fst	0	0	0.7617524	0.7617524
4	Fhy	0	0	0.7548869	0.7548869
5	Fb	0	0	0.2054667	0.2054667
6	Fet	0	0	0.2054667	0.2054667
7	Ft	0	0	0.0068655	0.0068655
8	Fm	0	0	0.0068655	0.0068655
9	T	1292.	1285.454	1292.	1285.454
10	P	1.382	0.982	1.382	0.982
11	Fi0	16.	16.	16.	16.
12	R	0.73	0.73	0.73	0.73
13	T0	1751.67	1751.67	1751.67	1751.67
14	P0	1.382	1.382	1.382	1.382
15	CT0	0.00108	0.00108	0.00108	0.00108
16	FT	20.	20.	20.96722	20.96722
17	Cst	0	0	2.799E-05	2.799E-05
18	Chy	0	0	2.773E-05	2.773E-05
19	Ceb	0.000216	0.0001112	0.000216	0.0001112
20	Kp1	0.028	0.028	0.028	0.028
21	Pst	0	0	0.0356513	0.0356513
22	Peb	0.2762033	0.141618	0.2762033	0.141618
23	Phy	0	0	0.03533	0.03533
24	r2b	0.169522	0.078762	0.169522	0.078762
25	r1st	0.6896026	0.236004	0.6896026	0.236004
26	r3t	0	0	0.0047949	0.0042912
27	Tr	77.	77.	77.	77.
28	deltaHr1eb	5.379E+04	5.379E+04	5.379E+04	5.379E+04
29	deltaHr2eb	3.843E+04	3.843E+04	3.852E+04	3.852E+04
30	Cpeb	73.24394	73.16032	73.24394	73.16032
31	Cpst	66.60199	66.53571	66.60199	66.53571
32	Cphy	7.29312	7.289302	7.29312	7.289302
33	Cpb	49.10628	49.0553	49.10628	49.0553
34	Cpet	20.79614	20.78039	20.79614	20.78039
35	Cpt	62.05723	61.98145	62.05723	61.98145
36	Cpm	49.13723	49.06145	49.13723	49.06145
37	Cpi0	448.1966	445.93	448.1966	445.93
38	deltaHr3eb	-2.055E+04	-2.056E+04	-2.055E+04	-2.056E+04

Differential equations

1 d(Feb)/d(L) = (-r1st - r2b - r3t) * 0.0885

Change in molarflowrate of ethylbenzene in the gas along the length of the tube in lbmol/hr*ft

2 d(Fst)/d(L) = r1st * 0.0885

Change in molarflowrate of styrene in the gas along the length of the tube in lbmol/hr*ft

3 d(Fhy)/d(L) = (r1st - r3t) * 0.0885

Change in molarflowrate of hydrogen in the gas along the length of the tube in lbmol/hr*ft

4 d(Fb)/d(L) = r2b * 0.0885

Change in molarflowrate of benzene in the gas along the length of the tube in lbmol/hr*ft

5 d(Fet)/d(L) = r2b * 0.0885

Change in molarflowrate of ethylene in the gas along the length of the tube in lbmol/hr*ft

6 d(Ft)/d(L) = r3t * 0.0885

Change in molarflowrate of toluene in the gas along the length of the tube in lbmol/hr*ft

7 d(Fm)/d(L) = r3t * 0.0885

Change in molarflowrate of methane in the gas along the length of the tube in lbmol/hr*ft

8 d(T)/d(L) = ((r1st * (-deltaHr1eb) + r2b * (-deltaHr2eb) + r3t * (-deltaHr3eb)) / (Feb * Cpeb + Fst * Cpst + Fhy * Cphy + Fb * Cpb + Fet * Cpet + Ft * Cpt + Fm * Cpm + Fi0 * Cpi0)) * 0.0885

Change in temperature of the gas along the length of the tube in Farenheit/ft

9 d(P)/d(L) = -0.02

Change in pressure of gas along the length of the tube in atm/ft

Explicit equations

1 Fi0 = 16

2 R = 0.73

Universal gas constant in cubicft*atm/lbmol*R

3 T0 = 1751.67

Initial temperature of the gas in Rankine

4 P0 = 1.382

Initial pressure of the gas in atm

5 CT0 = 0.00108

Initial concentration of the gas in lbmol/cubicft

6 FT = Feb + Fst + Fhy + Fb + Fet + Ft + Fm + Fi0

Total molarflowrate of the gas along the length of the tube in lbmol/hr

7 Cst = CT0 * Fst / FT * T0 / (T + 459.67) * P / P0

Concentration of styrene along the length of the tube in lbmol/cubicft

8 Chy = CT0 * Fhy / FT * T0 / (T + 459.67) * P / P0

Concentration of hydrogen along the length of the tube in lbmol/cubicft

9 Ceb = CT0 * Feb / FT * T0 / (T + 459.67) * P / P0

Concentration of ethylbenzene along the length of the tube in lbmol/cubicft

10 Kp1 = 0.028

Equilibrium constant for reaction 1 in atm

11 Pst = Cst * R * (T + 459.67)

Partial pressure of styrene in the gas along the length of the tube in atm

12 Peb = Ceb * R * (T + 459.67)

Partial pressure of ethylbenzene in the gas along the length of the tube in atm

13 Phy = Chy * R * (T + 459.67)

Partial pressure of hydrogen in the gas along the length of the tube in atm

14 r2b = 10 ^ ((-50800 / (4.575 * ((T + 459.67) / 1.8))) + 9.13) * Peb * 117

Rate of formation of benzene by reaction 2 in lbmol/cubicft*hr

15 r1st = 10 ^ ((-11370 / (4.575 * ((T + 459.67) / 1.8))) + 0.883) * (Peb - Pst * Phy / Kp1) * 117

Rate of formation of styrene by reaction 1 in lbmol/cubicft*hr

16 r3t = 10 ^ ((-21800 / (4.575 * ((T + 459.67) / 1.8))) + 2.78) * (Peb * Phy) * 117

Rate of formation of toluene by reaction 3 in lbmol/cubicft*hr

17 Tr = 77

Reference temperature in Farenheit

18 deltaHr1eb = 50580 + 5.83 * (T - Tr) - 0.00596 / 2 * (T ^ 2 - Tr ^ 2) + 0.151 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 1 with respect to ethybenzene in BTU/lbmolethylbenzene

19 deltaHr2eb = 45351 - 0.64 * (T - Tr) - 0.0034 / 2 * (T ^ 2 - Tr ^ 2) - 0.461 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 2 with respect to ethybenzene in BTU/lbmolethylbenzene

20 Cpeb = 26.18 + 0.0602 * T - 1.84 * 10 ^ (-5) * T ^ 2

Heat capacity of ethylbenzene in BTU/lbmol*F

21 Cpst = 25.12 + 0.0542 * T - 1.71 * 10 ^ (-5) * T ^ 2

Heat capacity of styrene in BTU/lbmol*F

22 Cphy = 6.89 + 3.94 * 10 ^ (-5) * T + 2.11 * 10 ^ (-7) * T ^ 2

Heat capacity of hydrogen in BTU/lbmol*F

23 Cpb = 16.29 + 0.0431 * T - 1.37 * 10 ^ (-5) * T ^ 2

Heat capacity of benzene in BTU/lbmol*F

24 Cpet = 9.25 + 0.0155 * T - 5.08 * 10 ^ (-6) * T ^ 2

Heat capacity of ethylene in BTU/lbmol*F

25 Cpt = 20.86 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of toluene in BTU/lbmol*F

26 Cpm = 7.94 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of methane in BTU/lbmol*F

27 Cpi0 = (3.470 + 1.450 * T) * 0.2388

28 deltaHr3eb = -23508 + 2.62 * (T - Tr) - 0.00024 / 2 * (T ^ 2 - Tr ^ 2) - 0.3 * 10 ^ (-7) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 3 with respect to ethybenzene in BTU/lbmolethylbenzene

General

Total number of equations	37
Number of differential equations	9
Number of explicit equations	28
Elapsed time	1.157 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

5.6 AN ALTERNATIVE DESIGN

An alternative design to the problem is two packed tube reactors in series with an heater in between.

5.6.1 THE POLYMATH PROGRAM FOR A TUBE IN THE FIRST REACTOR OF TWO PACKED TUBE REACTORS IN SERIES WITH A HEATER IN BETWEEN.

$dF_{EB}/dL = (-r_{1ST} - r_{2B} - r_{3T})\times117\times0.0885$; Change in molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$F_{EB}(0) = 4.0$, Initial molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$dF_{ST}/dL = r_{1ST}\times117\times0.0885$; Change in molarflowrate of styrene in the gas in lbmol/hr.ft

$F_{ST}(0) = 0$, Initial molarflowrate of styrene in the gas in lbmol/hr.ft

$dF_{H2}/dL = (r_{1ST} - r_{3T})\times117\times0.0885$; Change in molarflowrate of hydrogen in the gas in lbmol/hr.ft

$F_{H2}(0) = 0$, Initial molarflowrate of hydrogen in the gas in lbmol/hr.ft

$dF_B/dL = r_{2B}\times117\times0.0885$; Change in molarflowrate of benzene in the gas in lbmol/hr.ft

$F_B(0) = 0$, Initial molarflowrate of benzene in the gas in lbmol/hr.ft

$dF_{ET}/dL = r_{2B}\times117\times0.0885$; Change in molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$F_{ET}(0) = 0$, Initial molarflowrate of ethylbenzene in the gas in lbmol/hr.ft

$dF_T/dL = r_{3T}\times117\times0.0885$; Change in molarflowrate of toluene in the gas in lbmol/hr.ft

$F_T(0) = 0$, Initial molarflowrate of toluene in the gas in lbmol/hr.ft

$dF_M/dL = r_{3T}\times117\times0.0885$; Change in molarflowrate of methane in the gas in lbmol/hr.ft

$F_M(0) = 0$, Initial molarflowrate of methane in the gas in lbmol/hr.ft

$r_{1ST} = k_1(P_{EB} - P_SP_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3P_EP_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

$\mathrm{Log}_{10}k_1 = (-11370/4.575\times(T + 459.67)/1.8\ ^0K) + 0.883$

$\mathrm{Log}_{10}k_2 = (-50800/4.575\times(T + 459.67)/1.8\ ^0K) + 9.13$

$\mathrm{Log}_{10}k_3 = (-21800/4.575\times(T + 459.67)/1.8\ ^0K) + 2.78$

$P_{EB} = C_{EB}\times R\times(T + 459.67)$, Partial pressure of ethylbenzene in the gas in atm

$P_{ST} = C_{ST}\times R\times(T + 459.67)$, Partial pressure of styrene in the gas in atm

$P_T = C_T\times R\times(T + 459.67)$, Partial pressure of toluene in the gas in atm

$C_{EB} = C_{T0}\times F_{EB}/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of ethylbenzene along the length of the tube in $lbmol/ft^3$

$C_{ST} = C_{T0}\times F_{ST}/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of styrene along the length of the tube in $lbmol/ft^3$

$C_T = C_{T0}\times F_T/F_T\times T_0/(T + 459.67)\times P/P_0$, Concentration of toluene along the length of the tube in $lbmol/ft^3$

$K_1 = 0.028$, Equilibrium constant for reaction 1 in atm

$C_{T0} = 0.00108$, Initial concentration of the gas in $lbmol/ft^3$

$R = 0.73$, Universal gas constant in $ft^3\times atm/lbmol.^0R$

$F_T = F_{EB} + F_{ST} + F_{H2} + F_{ET} + F_T + F_M + F_{I0}$, Total molarflowrate of the gas in lbmol/hr

$T_0 = 1751.67$, Initial temperature of the gas in ^0R

$P_0 = 1.382$, Initial pressure of the gas in atm

T= Temperature of the gas in ^0F

P = Pressure of the gas in atm.

$dT/dL = (r_{1ST}\times(-deltaH_{r1EB}) + r_{2B}\times(-deltaH_{rEB}) + r_{3T}\times(-deltaH_{r3EB})/(F_{EB}\times C_{PEB} + F_{ST}\times C_{PST} + F_{H2}\times C_{PH2} + F_B\times C_{PB} + F_{ET}\times C_{PET} + F_T\times C_{PT} + F_M\times C_{PM} + F_{I0}\times C_{PI0})$

117×0.0885 Temperature drop across the length of the tube in $^0F/ft$

$T_0 = 1292\ ^0F$, Initial temperature of the gas

$deltaH_{r1EB} = 50580 + 5.83\times(T-T_R) - 0.00596/2\times(T^2 - T_R^2) + 0.151\times(10^{-5}/3)\times(T^3 - T_R^3)$, Heat of reaction 1 with respect to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r2EB} = 45351 - 0.64\times(T-T_R) - 0.0034/2\times(T^2 - T_R^2) -0.461\times(10^{-5}/3)\times(T^3 - T_R^3)$, Heat of reaction 2 with respect to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r3EB} = -23508 + 2.62\times(T-T_R) - 0.00024/2\times(T^2 - T_R^2) - 0.3\times(10^{-7}/3)\times(T^3 - T_R^3)$, Heat of reaction 3 with respect to ethylbenzene in

BTU/lbmolethylbenzene

$T_R = 77^0F$

$C_{PST} = 25.12 + 0.0542 \times T - 1.71 \times 10^{-5} \times T^2$, Heat capacity of styrene in BTU/lbmol.^{0}F

$C_{PEB} = 26.18 + 0.0602 \times T - 1.84 \times 10^{-5} \times T^2$,Heat capacity of ethylbenzene in BTU/lbmol^{0}F

$C_{PH2} = 6.89 + 3.94 \times 10^{-5} \times T + 2.11 \times 10^{-7} \times T^2$,Heat capacity of hydrogen in BTU/lbmol.^{0}F

$C_{PB} = 16.29 + 0.0431 \times T - 1.37 \times 10^{-5} \times T^2$, Heat capacity of benzene in BTU/lbmol.^{0}F

$C_{PET} = 9.25 + 0.0155 \times T - 5.08 \times 10^{-6} \times T^2$, Heat capacity of ethylene in BTU/lbmol.^{0}F

$C_{PT} = 20.86 + 0.0523 \times T - 1.58 \times 10^{-5} \times T^2$, Heat capacity of toluene in BTU/lbmol.^{0}F

$C_{PM} = 7.94 + 0.0602 \times T - 1.84 \times 10^{-5} \times T^2$, Heat capacity of methane in BTU/lbmol.^{0}F

$C_{PI0} = (3.470 + 1.450 \times T) \times 0.2388$, Heat capacity of steam in BTU/lbmol.^{0}F

$dP/dL = -0.02$, Pressure drop across the length of the tube in atm/ft

$P(0) = 1.382$ atm

$L(0) = 0$

$L(f) = 10$ ft

5.6.2 THE POLYMATH SOLUTION REPORT FOR A TUBE IN THE FIRST REACTOR OF TWO PACKED TUBE REACTORS IN SERIES WITH A HEATER IN BETWEEN IS GIVEN IN THE NEXT PAGE.

POLYMATH Report
Ordinary Differential Equations

No Title
13-May-2006

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	L	0	0	10.	10.
2	Feb	4.	3.391173	4.	3.391173
3	Fst	0	0	0.4839513	0.4839513
4	Fhy	0	0	0.4812017	0.4812017
5	Fb	0	0	0.1221258	0.1221258
6	Fet	0	0	0.1221258	0.1221258
7	Ft	0	0	0.0027496	0.0027496
8	Fm	0	0	0.0027496	0.0027496
9	T	1292.	1287.884	1292.	1287.884
10	P	1.382	1.182	1.382	1.182
11	Fi0	16.	16.	16.	16.
12	R	0.73	0.73	0.73	0.73
13	T0	1751.67	1751.67	1751.67	1751.67
14	P0	1.382	1.382	1.382	1.382
15	CT0	0.00108	0.00108	0.00108	0.00108
16	FT	20.	20.	20.60608	20.60608
17	Cst	0	0	2.175E-05	2.175E-05
18	Chy	0	0	2.162E-05	2.162E-05
19	Ceb	0.000216	0.0001524	0.000216	0.0001524
20	Kp1	0.028	0.028	0.028	0.028
21	Pst	0	0	0.0277405	0.0277405
22	Peb	0.2762033	0.1943851	0.2762033	0.1943851
23	Phy	0	0	0.0275829	0.0275829
24	r2b	0.169522	0.1121471	0.169522	0.1121471
25	r1st	0.6896026	0.4113602	0.6896026	0.4113602
26	r3t	0	0	0.0046715	0.0046715
27	Tr	77.	77.	77.	77.
28	deltaHr1eb	5.379E+04	5.379E+04	5.379E+04	5.379E+04
29	deltaHr2eb	3.843E+04	3.843E+04	3.848E+04	3.848E+04
30	Cpeb	73.24394	73.19155	73.24394	73.19155
31	Cpst	66.60199	66.56048	66.60199	66.56048
32	Cphy	7.29312	7.290717	7.29312	7.290717
33	Cpb	49.10628	49.07436	49.10628	49.07436
34	Cpet	20.79614	20.78629	20.79614	20.78629
35	Cpt	62.05723	62.00974	62.05723	62.00974
36	Cpm	49.13723	49.08974	49.13723	49.08974
37	Cpi0	448.1966	446.7715	448.1966	446.7715
38	deltaHr3eb	-2.055E+04	-2.056E+04	-2.055E+04	-2.056E+04

Differential equations

1 d(Feb)/d(L) = (-r1st - r2b - r3t) * 0.0885

Change in molarflowrate of ethylbenzene in the gas along the length of the tube in lbmol/hr*ft

2 d(Fst)/d(L) = r1st * 0.0885

Change in molarflowrate of styrene in the gas along the length of the tube in lbmol/hr*ft

3 d(Fhy)/d(L) = (r1st - r3t) * 0.0885

Change in molarflowrate of hydrogen in the gas along the length of the tube in lbmol/hr*ft

4 d(Fb)/d(L) = r2b * 0.0885

Change in molarflowrate of benzene in the gas along the length of the tube in lbmol/hr*ft

5 d(Fet)/d(L) = r2b * 0.0885

Change in molarflowrate of ethylene in the gas along the length of the tube in lbmol/hr*ft

6 d(Ft)/d(L) = r3t * 0.0885

Change in molarflowrate of toluene in the gas along the length of the tube in lbmol/hr*ft

7 d(Fm)/d(L) = r3t * 0.0885

Change in molarflowrate of methane in the gas along the length of the tube in lbmol/hr*ft

8 d(T)/d(L) = ((r1st * (-deltaHr1eb) + r2b * (-deltaHr2eb) + r3t * (-deltaHr3eb)) / (Feb * Cpeb + Fst * Cpst + Fhy * Cphy + Fb * Cpb + Fet * Cpet + Ft * Cpt + Fm * Cpm + Fi0 * Cpi0)) * 0.0885

Change in temperature of the gas along the length of the tube in Farenheit/ft

9 d(P)/d(L) = -0.02

Change in pressure of gas along the length of the tube in atm/ft

Explicit equations

1 Fi0 = 16

2 R = 0.73

Universal gas constant in cubicft*atm/lbmol*R

3 T0 = 1751.67

Initial temperature of the gas in Rankine

4 P0 = 1.382

Initial pressure of the gas in atm

5 CT0 = 0.00108

Initial concentration of the gas in lbmol/cubicft

6 FT = Feb + Fst + Fhy + Fb + Fet + Ft + Fm + Fi0

Total molarflowrate of the gas along the length of the tube in lbmol/hr

7 Cst = CT0 * Fst / FT * T0 / (T + 459.67) * P / P0

Concentration of styrene along the length of the tube in lbmol/cubicft

8 Chy = CT0 * Fhy / FT * T0 / (T + 459.67) * P / P0

Concentration of hydrogen along the length of the tube in lbmol/cubicft

9 Ceb = CT0 * Feb / FT * T0 / (T + 459.67) * P / P0

Concentration of ethylbenzene along the length of the tube in lbmol/cubicft

10 Kp1 = 0.028

Equilibrium constant for reaction 1 in atm

11 Pst = Cst * R * (T + 459.67)

Partial pressure of styrene in the gas along the length of the tube in atm

12 Peb = Ceb * R * (T + 459.67)

Partial pressure of ethylbenzene in the gas along the length of the tube in atm

13 Phy = Chy * R * (T + 459.67)

Partial pressure of hydrogen in the gas along the length of the tube in atm

14 r2b = 10 ^ ((-50800 / (4.575 * ((T + 459.67) / 1.8))) + 9.13) * Peb * 117

Rate of formation of benzene by reaction 2 in lbmol/cubicft*hr

15 r1st = 10 ^ ((-11370 / (4.575 * ((T + 459.67) / 1.8))) + 0.883) * (Peb - Pst * Phy / Kp1) * 117

Rate of formation of styrene by reaction 1 in lbmol/cubicft*hr

16 r3t = 10 ^ ((-21800 / (4.575 * ((T + 459.67) / 1.8))) + 2.78) * (Peb * Phy) * 117

Rate of formation of toluene by reaction 3 in lbmol/cubicft*hr

17 Tr = 77

Reference temperature in Farenheit

18 deltaHr1eb = 50580 + 5.83 * (T - Tr) - 0.00596 / 2 * (T ^ 2 - Tr ^ 2) + 0.151 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 1 with respect to ethybenzene in BTU/lbmolethylbenzene

19 deltaHr2eb = 45351 - 0.64 * (T - Tr) - 0.0034 / 2 * (T ^ 2 - Tr ^ 2) - 0.461 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 2 with respect to ethybenzene in BTU/lbmolethylbenzene

20 Cpeb = 26.18 + 0.0602 * T - 1.84 * 10 ^ (-5) * T ^ 2

Heat capacity of ethylbenzene in BTU/lbmol*F

21 Cpst = 25.12 + 0.0542 * T - 1.71 * 10 ^ (-5) * T ^ 2

Heat capacity of styrene in BTU/lbmol*F

22 Cphy = 6.89 + 3.94 * 10 ^ (-5) * T + 2.11 * 10 ^ (-7) * T ^ 2

Heat capacity of hydrogen in BTU/lbmol*F

23 Cpb = 16.29 + 0.0431 * T - 1.37 * 10 ^ (-5) * T ^ 2

Heat capacity of benzene in BTU/lbmol*F

24 Cpet = 9.25 + 0.0155 * T - 5.08 * 10 ^ (-6) * T ^ 2

Heat capacity of ethylene in BTU/lbmol*F

25 Cpt = 20.86 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of toluene in BTU/lbmol*F

26 Cpm = 7.94 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of methane in BTU/lbmol*F

27 Cpi0 = (3.470 + 1.450 * T) * 0.2388

28 deltaHr3eb = -23508 + 2.62 * (T - Tr) - 0.00024 / 2 * (T ^ 2 - Tr ^ 2) - 0.3 * 10 ^ (-7) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 3 with respect to ethybenzene in BTU/lbmolethylbenzene

General

Total number of equations	37
Number of differential equations	9
Number of explicit equations	28
Elapsed time	1.157 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

5.6.3 THE POLYMATH PROGRAM FOR A TUBE IN THE SECOND REACTOR OF TWO PACKED TUBE REACTORS IN SERIES WITH A HEATER IN BETWEEN.

$dF_{EB}/dL = (-r_{1ST} - r_{2B} - r_{3T})\times117\times0.0885$; Change in molarflowrate of ethylbenzene along the tube length in lbmol/hr.ft

$F_{EB}(0) = 3.391$,Initial molarflowrate of ethylbenzene in lbmol/hr.ft

$dF_{ST}/dL = r_{1ST}\times117\times0.0885$; Change in molarflowrate of styrene along the tube length in lbmol/hr.ft

$F_{ST}(0) = 0.484$, Initial molarflowrate of styrene in lbmol/hr.ft

$dF_{H2}/dL = (r_{1ST} - r_{3T})\times117\times0.0885$; Change of molarflowrate of hydrogen along the tube length in lbmol/hr.ft

$F_{H2}(0) = 0.481$, Initial molarflowrate of hydrogen in lbmol/hr.ft

$dF_{B}/dL = r_{2B}\times117\times0.0885$; Change of molarflowrate of benzene along the tube length in lbmol/hr.ft

$F_{B}(0) = 0.122$, Initial molarflowrate of benzene in lbmol/hr.ft

$dF_{ET}/dL = r_{2B}\times117\times0.0885$; Change of molarflowrate of ethylbenzene along the tube length in lbmol/hr.ft

$F_{ET}(0) = 0.122$, Inital molarflowrate of ethylbenzene in lbmol/hr.ft

$dF_{T}/dL = r_{3T}\times117\times0.0885$; Change of molarflowrate of toluene along the tube length in lbmol/hr.ft

$F_{T}(0) = 0.002$, Initial molarflowrate of toluene in lbmol/hr.ft

$dF_{M}/dL = r_{3T}\times117\times0.0885$; Change of molarflowrate of methane along the tube length in lbmol/hr.ft

$F_{M}(0) = 0.002$, Initial molarflowrate of methane in lbmol/hr.ft

$r_{1ST} = k_1(P_{EB} - P_S P_{H2}/K_1)$, rate of formation of styrene in lbmol/hr.lbcat

$r_{2B} = k_2 P_{EB}$, rate of formation of benzene in lbmol/hr.lbcat

$r_{3T} = k_3 P_E P_{H2}$, rate of formation of toluene in lbmol/hr.lbcat

$\mathrm{Log}_{10}k_1 = (-11370/4.575\times(T + 459.67)/1.8\ {}^0K) + 0.883$

$\mathrm{Log}_{10}k_2 = (-50800/4.575\times(T + 459.67)/1.8\ {}^0K) + 9.13$

$\mathrm{Log}_{10}k_3 = (-21800/4.575\times(T + 459.67)/1.8\ {}^0K) + 2.78$

$P_{EB} = C_{EB}\times R\times(T + 459.67)$, Partial pressure of ethylbenzene in the gas in atm

$P_{ST} = C_{ST}\times R\times(T + 459.67)$, Partial pressure of styrene in the gas in atm

$P_T = C_T×R×(T + 459.67)$, Partial pressure of toluene in the gas in atm

$C_{EB} = C_{T0}×F_{EB}/F_T×T_0/(T + 459.67)×P/P_0$, Concentration of ethylbenzene along the length of the tube in lbmol/ft^3

$C_{ST} = C_{T0}×F_{ST}/F_T×T_0/(T + 459.67)×P/P_0$, Concentration of styrene along the length of the tube in lbmol/ft^3

$C_T = C_{T0}×F_T/F_T×T_0/(T + 459.67)×P/P_0$, Concentration of toluene along the length of the tube in lbmol/ft^3

$K_{P1} = 0.028$, Equilibrium constant for reaction 1 in atm

$C_{T0} = 0.000879$, Initial concentration of the gas in lbmol/ft^3

$R = 0.73$, Universal gas constant in ft^3×atm/lbmol.^{0}R

$F_T = F_{EB} + F_{ST} + F_{H2} + F_{ET} + F_T + F_M + F_{I0}$, Total molarflowrate of the gas in lbmol/hr

$F_{I0} = 16$lbmol/hr

$T_0 = 1841.67$, Initial temperature of the gas in ^{0}R

$P_0 = 1.182$, Initial pressure of the gas in atm

T= Temperature of the gas in ^{0}F

P = Pressure of the gas in atm.

$dT/dL = (r_{1ST}×(-deltaH_{r1EB}) + r_{2B}×(-deltaH_{rEB}) + r_{3T}×(-deltaH_{r3EB}))×117/(F_{EB}×C_{PEB} + F_{ST}×C_{PST} + F_{H2}×C_{PH2} + F_B×C_{PB} + F_{ET}×C_{PET} + F_T×C_{PT} + F_M×C_{PM} +F_{I0}×C_{PI0}) × 0.0885$, Temperature drop across the length of the tube in ^{0}F/ft

$deltaH_{r1EB} = 50580 + 5.83×(T-T_R) – 0.00596/2×(T^2 – T_R^2) + 0.151×(10^{-5}/3)×(T^3 – T_R^3)$, Heat of reaction 1 with respevt to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r2EB} = 45351 – 0.64×(T-T_R) – 0.0034/2×(T^2 – T_R^2) -0.461×(10^{-5}/3)×(T^3 – T_R^3)$,Heat of reaction 2 with respect to ethylbenzene in BTU/lbmolethylbenzene

$deltaH_{r3EB} = -23508 + 2.62×(T-T_R) – 0.00024/2×(T^2 – T_R^2) - 0.3×(10^{-7}/3)×(T^3 – T_R^3)$,Heat of reaction 3 with respect to ethylbenzene in BTU/lbmolethylbenzene

$T_R = 77^0$F

$C_{PST} = 25.12 + 0.0542×T – 1.71×10^{-5}×T^2$, Heat capacity of styrene in BTU/lbmol.^{0}F

C_{PEB}=26.18 + 0.0602×T – 1.84×10^{-5}×T^2,Heat capacity of ethylbenzene in BTU/lbmol^{0}F

C_{PH2}= 6.89 + 3.94×10^{-5}×T + 2.11×10^{-7}×T^2 , Heat capacity of hydrogen in BTU/lbmol.^{0}F

C_{PB} = 16.29 + 0.0431×T – 1.37×10^{-5}×T^2 , Heat capacity of benzene in BTU/lbmol.^{0}F

C_{PET} = 9.25 + 0.0155×T – 5.08×10^{-6}×T^2 , Heat capacity of ethylene in BTU/lbmol.^{0}F

C_{PT} = 20.86 + 0.0523×T – 1.58×10^{-5}×T^2 , Heat capacity of toluene in BTU/lbmol.^{0}F

C_{PM} = 7.94 + 0.0602×T – 1.84×10^{-5}×T^2 , Heat capacity of methane in BTU/lbmol.^{0}F

C_{PI0} = (3.470 + 1.450×T)×0.2388 , Heat capacity of steam in BTU/lbmol.^{0}F

dP/dL = -0.02 , Pressure drop across the length of the tube in atm/ft

P(0) = 1.182 atm

L(0) = 0

L(f) = 10 ft

5.6.4 THE POLYMATH SOLUTION REPORT FOR A TUBE IN THE SECOND REACTOR OF TWO PACKED BED REACTORS IN SERIES WITH A HEATER IN BETWEEN.

POLYMATH Report
Ordinary Differential Equations

No Title
13-May-2006

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	L	0	0	10.	10.
2	Feb	3.391	2.746648	3.391	2.746648
3	Fst	0.484	0.484	0.8204464	0.8204464
4	Fhy	0.481	0.481	0.8102164	0.8102164
5	Fb	0.122	0.122	0.4226757	0.4226757
6	Fet	0.122	0.122	0.4226757	0.4226757
7	Ft	0.002	0.002	0.00923	0.00923
8	Fm	0.002	0.002	0.00923	0.00923
9	T	1382.	1378.334	1382.	1378.334
10	P	1.182	0.982	1.182	0.982
11	Fi0	16.	16.	16.	16.
12	R	0.73	0.73	0.73	0.73
13	T0	1841.67	1841.67	1841.67	1841.67
14	P0	1.182	1.182	1.182	1.182
15	CT0	0.000879	0.000879	0.000879	0.000879
16	FT	20.604	20.604	21.24112	21.24112
17	Cst	2.065E-05	2.065E-05	2.826E-05	2.826E-05
18	Chy	2.052E-05	2.052E-05	2.791E-05	2.791E-05
19	Ceb	0.0001447	9.462E-05	0.0001447	9.462E-05
20	Kp1	0.028	0.028	0.028	0.028
21	Pst	0.0277599	0.0277599	0.0379219	0.0379219
22	Peb	0.1944911	0.126953	0.1944911	0.126953
23	Phy	0.0275878	0.0275878	0.0374491	0.0374491
24	r2b	0.4310205	0.2676665	0.4310205	0.2676665
25	r1st	0.5562267	0.2508844	0.5562267	0.2508844
26	r3t	0.0083289	0.0072238	0.0085888	0.0072238
27	Tr	77.	77.	77.	77.
28	deltaHr1eb	5.384E+04	5.384E+04	5.384E+04	5.384E+04
29	deltaHr2eb	3.722E+04	3.722E+04	3.728E+04	3.728E+04
30	Cpeb	74.2338	74.1993	74.2338	74.1993
31	Cpst	67.3647	67.33904	67.3647	67.33904
32	Cphy	7.347445	7.345165	7.347445	7.345165
33	Cpb	49.68824	49.66887	49.68824	49.66887
34	Cpet	20.96859	20.96317	20.96859	20.96317
35	Cpt	62.9618	62.92995	62.9618	62.92995
36	Cpm	50.0418	50.00995	50.0418	50.00995
37	Cpi0	479.36	478.0905	479.36	478.0905
38	deltaHr3eb	-2.034E+04	-2.035E+04	-2.034E+04	-2.035E+04

Differential equations

1 d(Feb)/d(L) = (-r1st - r2b - r3t) * 0.0885

Change in molarflowrate of ethylbenzene in the gas along the length of the tube in lbmol/hr*ft

2 d(Fst)/d(L) = r1st * 0.0885

Change in molarflowrate of styrene in the gas along the length of the tube in lbmol/hr*ft

3 d(Fhy)/d(L) = (r1st - r3t) * 0.0885

Change in molarflowrate of hydrogen in the gas along the length of the tube in lbmol/hr*ft

4 d(Fb)/d(L) = r2b * 0.0885

Change in molarflowrate of benzene in the gas along the length of the tube in lbmol/hr*ft

5 d(Fet)/d(L) = r2b * 0.0885

Change in molarflowrate of ethylene in the gas along the length of the tube in lbmol/hr*ft

6 d(Ft)/d(L) = r3t * 0.0885

Change in molarflowrate of toluene in the gas along the length of the tube in lbmol/hr*ft

7 d(Fm)/d(L) = r3t * 0.0885

Change in molarflowrate of methane in the gas along the length of the tube in lbmol/hr*ft

8 d(T)/d(L) = ((r1st * (-deltaHr1eb) + r2b * (-deltaHr2eb) + r3t * (-deltaHr3eb)) / (Feb * Cpeb + Fst * Cpst + Fhy * Cphy + Fb * Cpb + Fet * Cpet + Ft * Cpt + Fm * Cpm + Fi0 * Cpi0)) * 0.0885

Change in temperature of the gas along the length of the tube in Farenheit/ft

9 d(P)/d(L) = -0.02

Change in pressure of gas along the length of the tube in atm/ft

Explicit equations

1 Fi0 = 16

2 R = 0.73

Universal gas constant in cubicft*atm/lbmol*R

3 T0 = 1841.67

Initial temperature of the gas in Rankine

4 P0 = 1.182

Initial pressure of the gas in atm

5 CT0 = 0.000879

Initial concentration of the gas in lbmol/cubicft

6 FT = Feb + Fst + Fhy + Fb + Fet + Ft + Fm + Fi0

Total molarflowrate of the gas along the length of the tube in lbmol/hr

7 Cst = CT0 * Fst / FT * T0 / (T + 459.67) * P / P0

Concentration of styrene along the length of the tube in lbmol/cubicft

8 Chy = CT0 * Fhy / FT * T0 / (T + 459.67) * P / P0

Concentration of hydrogen along the length of the tube in lbmol/cubicft

9 Ceb = CT0 * Feb / FT * T0 / (T + 459.67) * P / P0

Concentration of ethylbenzene along the length of the tube in lbmol/cubicft

10 Kp1 = 0.028

Equilibrium constant for reaction 1 in atm

11 Pst = Cst * R * (T + 459.67)

Partial pressure of styrene in the gas along the length of the tube in atm

12 Peb = Ceb * R * (T + 459.67)

Partial pressure of ethylbenzene in the gas along the length of the tube in atm

13 Phy = Chy * R * (T + 459.67)

Partial pressure of hydrogen in the gas along the length of the tube in atm

14 r2b = 10 ^ ((-50800 / (4.575 * ((T + 459.67) / 1.8))) + 9.13) * Peb * 117

Rate of formation of benzene by reaction 2 in lbmol/cubicft*hr

15 r1st = 10 ^ ((-11370 / (4.575 * ((T + 459.67) / 1.8))) + 0.883) * (Peb - Pst * Phy / Kp1) * 117

Rate of formation of styrene by reaction 1 in lbmol/cubicft*hr

16 r3t = 10 ^ ((-21800 / (4.575 * ((T + 459.67) / 1.8))) + 2.78) * (Peb * Phy) * 117

Rate of formation of toluene by reaction 3 in lbmol/cubicft*hr

17 Tr = 77

Reference temperature in Farenheit

18 deltaHr1eb = 50580 + 5.83 * (T - Tr) - 0.00596 / 2 * (T ^ 2 - Tr ^ 2) + 0.151 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 1 with respect to ethybenzene in BTU/lbmolethylbenzene

19 deltaHr2eb = 45351 - 0.64 * (T - Tr) - 0.0034 / 2 * (T ^ 2 - Tr ^ 2) - 0.461 * 10 ^ (-5) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 2 with respect to ethybenzene in BTU/lbmolethylbenzene

20 Cpeb = 26.18 + 0.0602 * T - 1.84 * 10 ^ (-5) * T ^ 2

Heat capacity of ethylbenzene in BTU/lbmol*F

21 Cpst = 25.12 + 0.0542 * T - 1.71 * 10 ^ (-5) * T ^ 2

Heat capacity of styrene in BTU/lbmol*F

22 Cphy = 6.89 + 3.94 * 10 ^ (-5) * T + 2.11 * 10 ^ (-7) * T ^ 2

Heat capacity of hydrogen in BTU/lbmol*F

23 Cpb = 16.29 + 0.0431 * T - 1.37 * 10 ^ (-5) * T ^ 2

Heat capacity of benzene in BTU/lbmol*F

24 Cpet = 9.25 + 0.0155 * T - 5.08 * 10 ^ (-6) * T ^ 2

Heat capacity of ethylene in BTU/lbmol*F

25 Cpt = 20.86 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of toluene in BTU/lbmol*F

26 Cpm = 7.94 + 0.0523 * T - 1.58 * 10 ^ (-5) * T ^ 2

Heat capacity of methane in BTU/lbmol*F

27 Cpi0 = (3.470 + 1.450 * T) * 0.2388

28 deltaHr3eb = -23508 + 2.62 * (T - Tr) - 0.00024 / 2 * (T ^ 2 - Tr ^ 2) - 0.3 * 10 ^ (-7) / 3 * (T ^ 3 - Tr ^ 3)

Heat of reaction 3 with respect to ethybenzene in BTU/lbmolethylbenzene

General

Total number of equations	37
Number of differential equations	9
Number of explicit equations	28
Elapsed time	1.157 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

CHAPTER 6
RESULTS AND DISCUSSION

6.1 For a single packed bed reactor

The inlet molar flowrate of ethylbenzene = F_{EB0} = 4 lbmol/hr

The outlet molar flowrate of ethylbenzene = F_{EB} = 3.026 lbmol/hr

The conversion of ethylbenzene = X = moles E reacted/moles E fed

$= (F_{EB0} - F_{EB})/F_{EB0}$

= 0.243

The inlet molar flowrate of styrene = $F_{ST0} = 0$

The outlet flowrate of styrene = F_{ST} = 0.762 lbmol/hr

The yield of styrene = Y = moles S produced/moles E reacted

$= F_{ST}/(F_{EB0} - F_{EB})$

= 0.782

The inlet temperature of gas mixture = T_0 = 1292 ^{0}F

The outlet temperature of the gas mixture = T= 1285.45 ^{0}F

The inlet pressure of the gas mixture = P_0 = 1.382 atm

The outlet pressure of the gas mixture = P = 0.982 atm

Moles of styrene produced per hour = 0.762 lbmol/hr

Moles of styrene produced per year = 6096 lbmol/yr

One year = 8000 hours

Mol.Wt of styrene = 104 lb

Pounds of styrene produced per year = 633984 lb/yr

Number of tubes required to produce 20 million pounds per year =

$2\times10^7/417664 = 31.54 = 32$

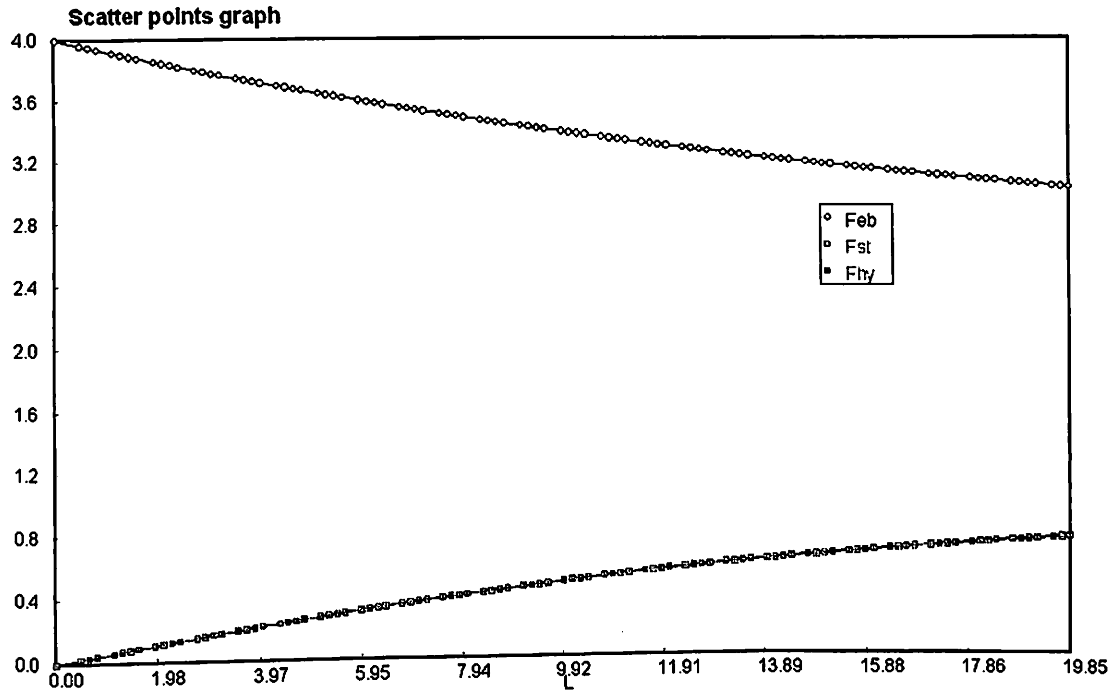
Total length of the tubes = 640 ft

The volume of reactor required = $0.0885\times20\times32 = 56.64 = 57$ ft^3

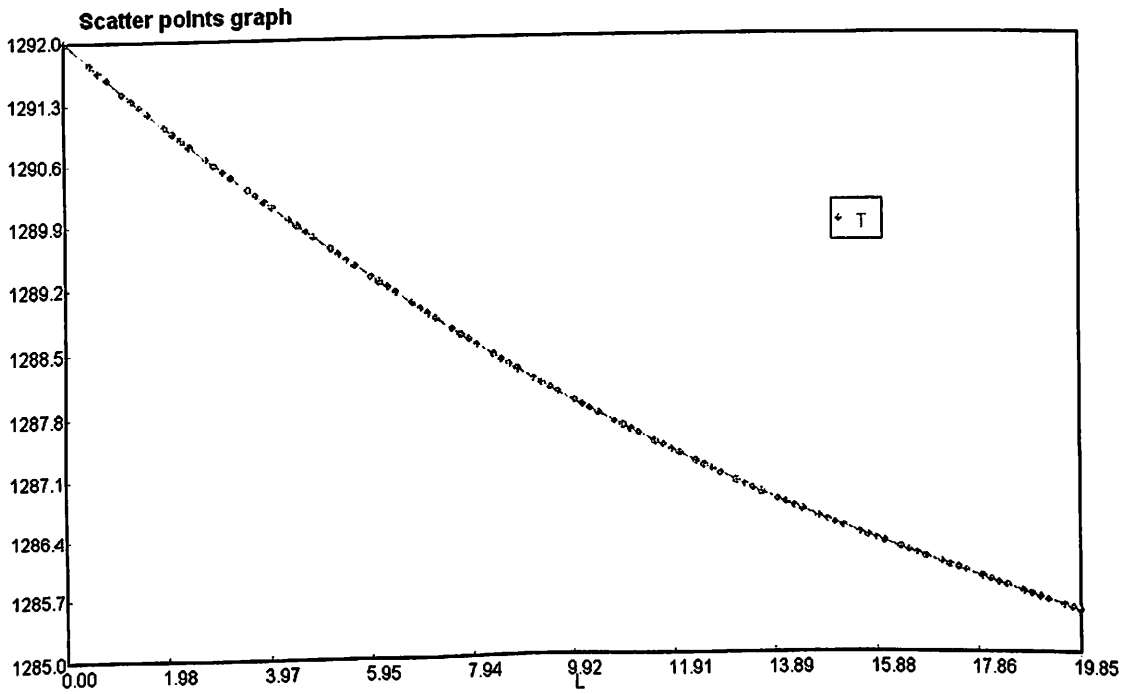
Density of catalyst bed = 61 lb/ft^3

The mass of catalyst required = $57\times61 = 3477$ lb

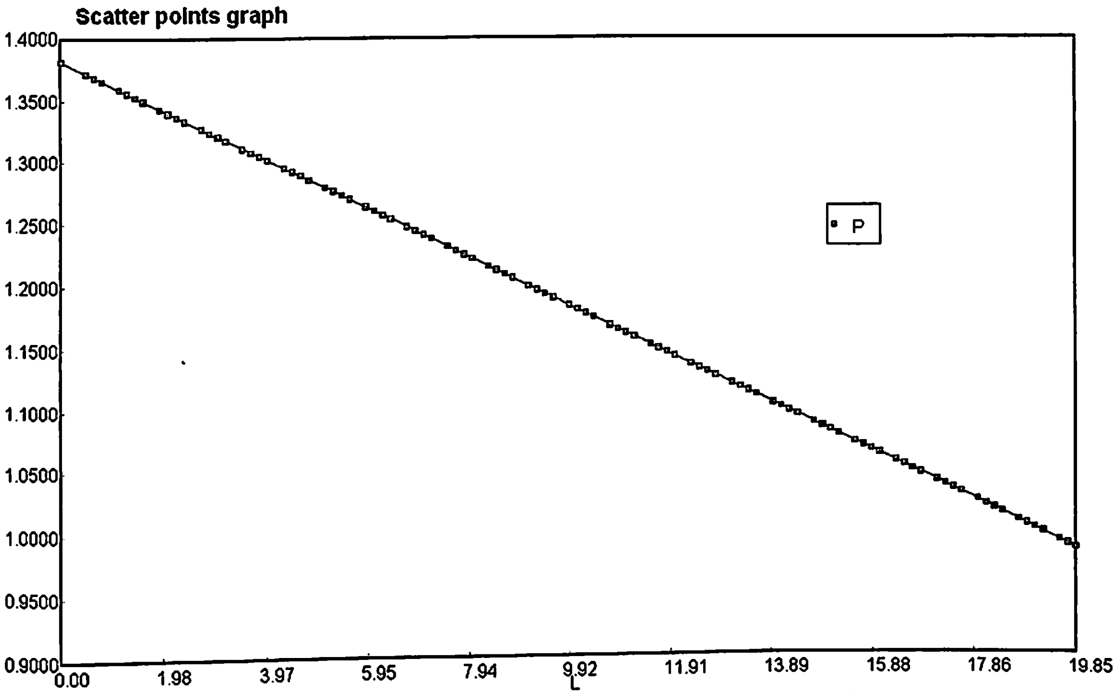
The plots of molarflowrates of ethylbenzene , styrene and hydrogen along the tube length are included with the plots of temperature and pressure from the next page



Molar flowrates of ethylbenzene, styrene and hydrogen in lbmol/hr vs length of the tube for a tube in ft in a single reactor



Temperature of the gas in ^{0}F vs length of the tube for a tube in ft in a single reactor



Pressure of the gas in atm vs length of the tube in ft in a single reactor

6.2 For two packed bed rectors in series with a heater in between

For a single tube in the first reactor of the two packed bed reactors in series with a heater in between:

The inlet molar flowrate of ethylbenzene = F_{EB0} = 4 lbmol/hr
The outlet molar flowrate of ethylbenzene = F_{EB} = 3.391 lbmol/hr
The conversion of ethylbenzene = X = moles E reacted/moles E fed
= $(F_{EB0} - F_{EB})/F_{EB0}$
= 0.152
The inlet molar flowrate of styrene = F_{ST0} = 0
The outlet flowrate of styrene = F_{ST} = 0.484 lbmol/hr
The yield of styrene = Y = moles S produced/moles E reacted
= $F_{ST}/(F_{EB0} - F_{EB})$
= 0.795
The inlet temperature of gas mixture = T_0 = 1292 ^{0}F
The outlet temperature of the gas mixture = T= 1287.88 ^{0}F
The inlet pressure of the gas mixture = P_0 = 1.382 atm
The outlet pressure of the gas mixture = P = 1.182 atm

Since we do not have any information about the heater in between, let's assume the products of reactor 1 are heated to a temperature of 1382^{0}F

For a single tube in the second reactor of the two packed bed reactors in series with a heater in between:

The inlet molar flowrate of ethylbenzene = F_{EB0} = 3.391 lbmol/hr
The outlet molar flowrate of ethylbenzene = F_{EB} = 2.745 lbmol/hr
The conversion of ethylbenzene = X = moles E reacted/moles E fed
= $(F_{EB0} - F_{EB})/F_{EB0}$
= 0.31
The inlet molar flowrate of styrene = F_{ST0} = 0.484 lbmol/hr
The outlet flowrate of styrene = F_{ST} = 0.820 lbmol/hr

The yield of styrene = Y = moles S produced/moles E reacted

$= (F_{ST} - F_{ST0})/(F_{EB0} - F_{EB})$

$= 0.52$

The inlet temperature of gas mixture = T_0 = 1382.67 ^{0}F

The outlet temperature of the gas mixture = T= 1378.69 ^{0}F

The inlet pressure of the gas mixture = P_0 = 1.182 atm

The outlet pressure of the gas mixture = P = 0.982 atm

The overall conversion of ethylbenzene = (4 – 2.746)/4 = 0.31

The overall yield of styrene = 0.57362/(4 – 1.6608) = 0.65

Moles of styrene produced per hour by two reactors in series = 0.820 lbmol/hr

Moles of styrene produced per year = 6560 lbmol/yr

One year = 8000 hours

Mol.Wt of styrene = 104 lb

Pounds of styrene produced per year = 682240 lb/yr

Number of tubes required to produce 20 million pounds per year = $2\times10^7/477251.84$ = 28.31 = 29

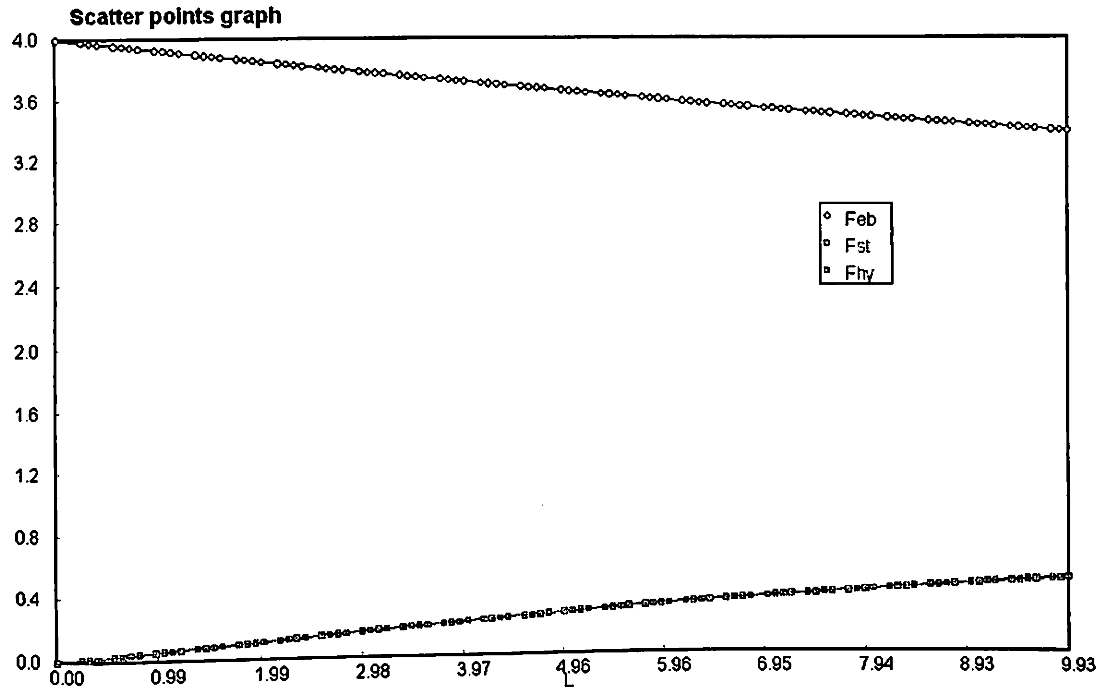
Total length of the tubes = 580 ft

Volume of reactor required = 0.0885×20×29 = 51.33= 52 ft^3

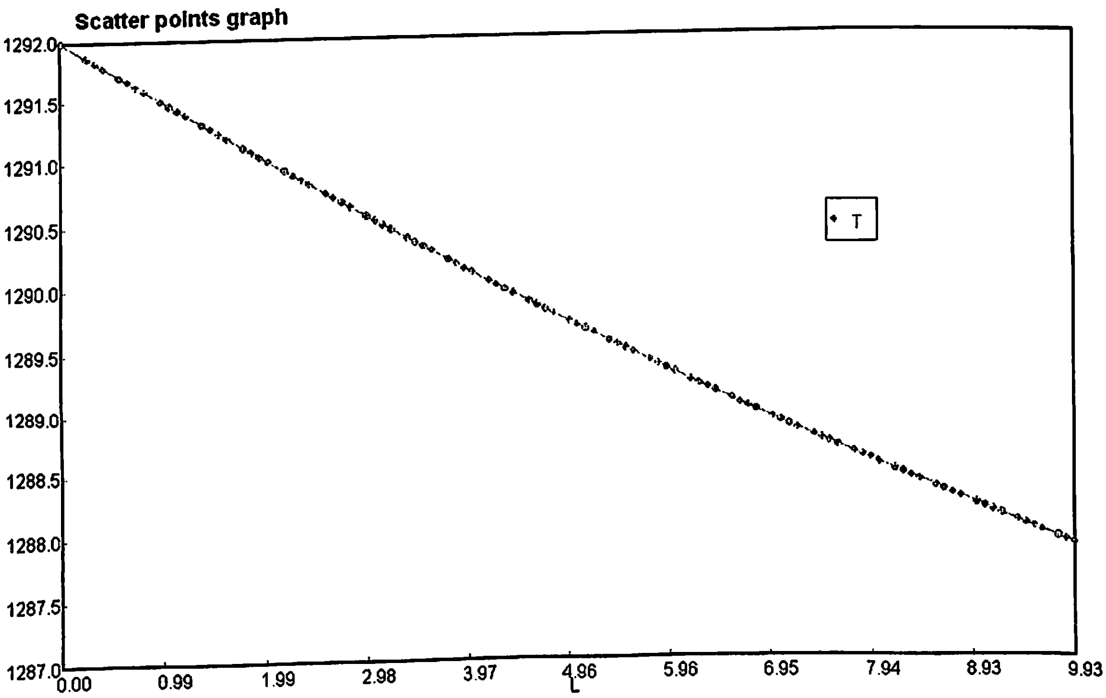
Density of catalyst bed = 61 lb/ft^3

Mass of catalyst required = 75×61 = 3172 lb

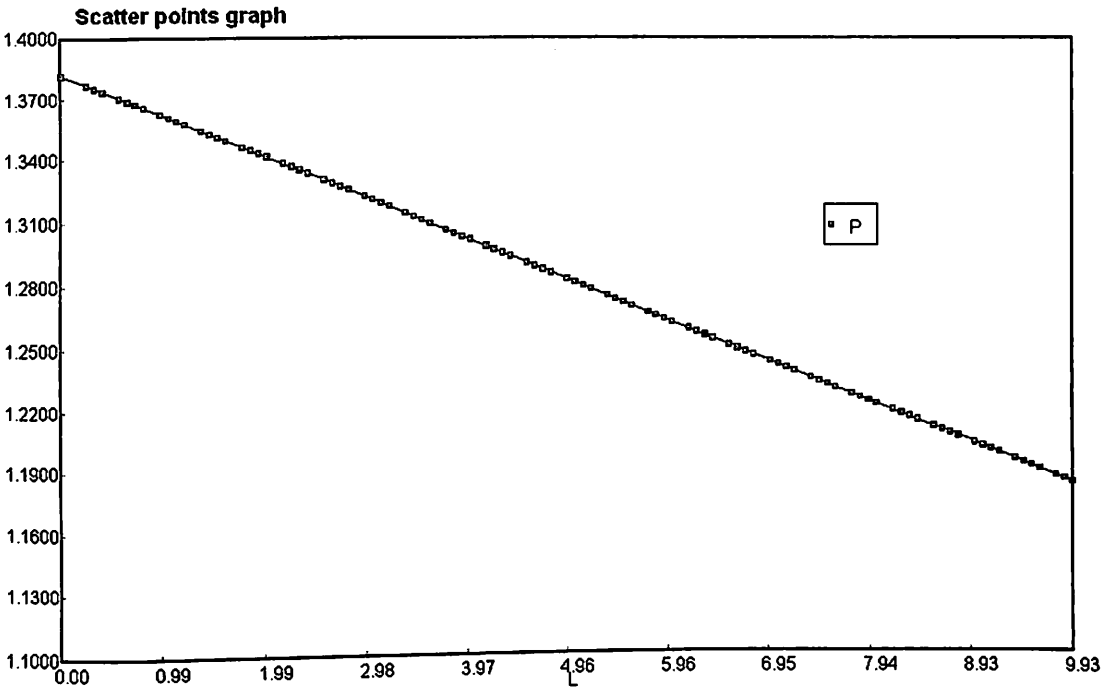
The plots of molarflowrates of ethylbenzene , styrene and hydrogen along with the plots of temperature and pressure along the tube length are included from the next page



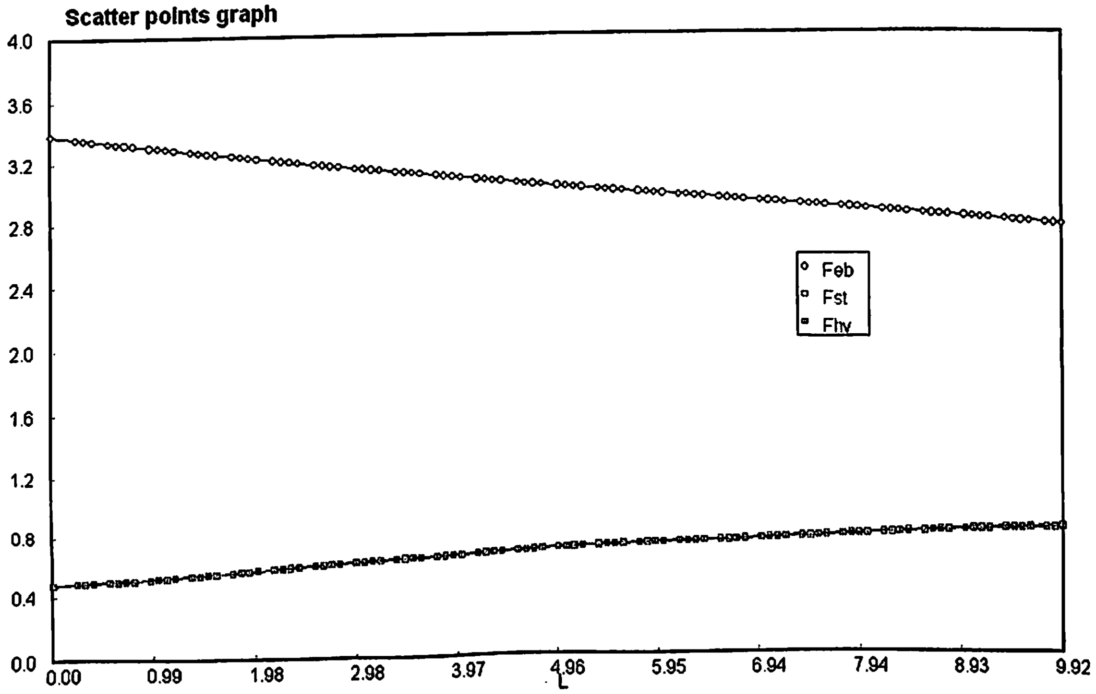
Molarflowrates of ethylbenzene, styrene and hydrogen in lbmol/hr vs length of the tube for a tube in ft in a single tube in the first reactor of two packed tube reactors in series



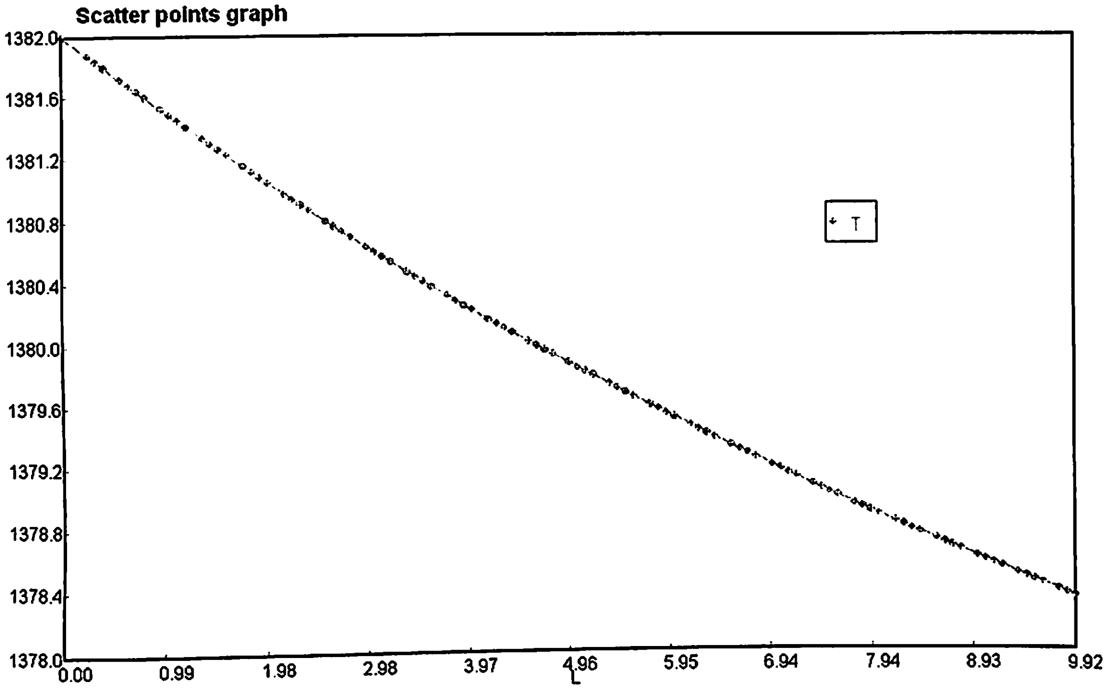
Temperature of the gas in ^{0}F vs length of the tube for a tube in ft in a single tube in the first reactor of two packed tube reactors in series



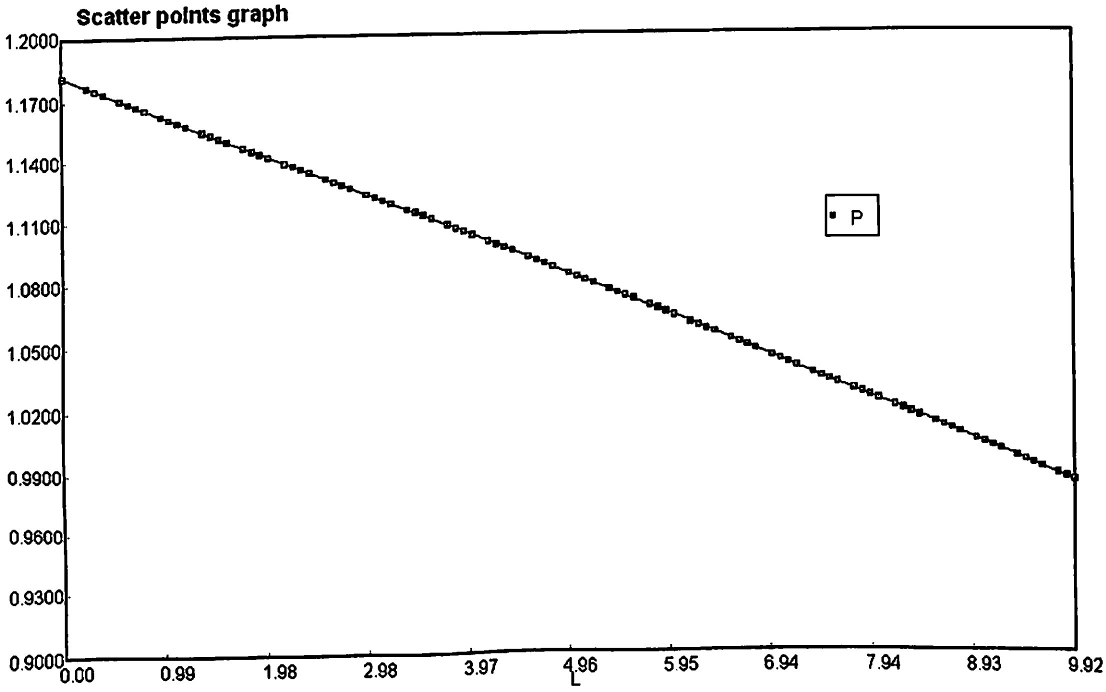
Pressure of the gas in atm vs length of the tube for a tube in ft in a single tube in the first reactor of two packed tube reactors in series



Molarflowrates of ethylbenzene, styrene and hydrogen in lbmol/hr vs length of the tube for a tube in ft in a single tube in the second reactor of two packed tube reactors in series



Temperature of the gas in ^{0}F vs length of the tube for a tube in ft in a single tube in the second reactor of two packed tube reactors in series



Pressure of the gas in atm vs length of the tube for a tube in ft in a single tube in the second reactor of two packed tube reactors in series

The conversion of ethylbenzene is greater for reactors in series than a single reactor. The amount of styrene produced by reactors in series is greater than the amount produced by a single reactor. The number of tubes and hence the volume of catalyst required is less for reactors in series than a single reactor.

Nonetheless the yield of styrene is less in reactors in series than a single reactor. This is because high operating temperatures as taken in this project favors side reactions and hence less yield.

Moreover the operating cost of heater in between the reactors in series has to be considered before selecting the reactor system. This additional cost is not there for a single reactor. The extra cost for the single reactor is the fixed cost of the extra tubes required for producing the same amount of styrene as reactors in series.

This means with respect to conversion and number of tubes required for the same amount of production of styrene the reactors is series is favoured while with repect to the operating costs and yield of styrene the single reactor is favourable.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

The reactor has been modeled using ideal gas behavior and plug flow. The conversion for single reactor is found to be roughly 25 % which is close to 30 % as reported in the reference http:// cheweb. tamu. edu. The design for styrene production at 20 million pounds per year is done and the number of tubes required is found to be 32. However the conversion increases to 31% and number of tubes decreases when two packed tube reactors are used with a heater in between.

The operating cost of heater is to be considered before selecting a reactor system. Hence it is recommended to do an economic study to find the optimum design for the reactor.

NOMENCLATURE FOR CATALYTIC STYRENE MANUFACTURE

r_1 reaction rate, lb moles/(hr) (lb cat), for formation of styrene by eq. 1; r_2 for eq. 2; r_3 for eq. 3

k_1 rate constant, lb moles/(hr)(atm)(lb cat), for styrene formation; k_2 for eq. 2; k_3 for eq. 3

P_{EB} partial pressure, atm, ethylbenzene

P_S partial pressure, atm, styrene

P_{H2} partial pressure, atm, hydrogen

K_1 equilibrium constant for styrene formation, atm

T ^{0}K reaction temperature in Arrhenius equation, K

T(z) reactor temperature as a function of position, ^{0}F

T_0 reactor feed temperature, ^{0}F

T_{fg} flue gas temperature, ^{0}F (assume constant.)

X fractional conversion to ethylbenzene, lb moles EB react/lb mole EB fed

Y yield of styrene (S), lb moles S formed/lb mole EB reacted

Z yield of toluene (T), lb moles T formed/lb mole EB reacted

Cpi(T) heat capacity of the ith component, BTU/(lb-mol ^{0}F)

L catalyst depth, feet

F feed to reactor, lb moles/hr

W catalyst weight, lb, dW differential catalyst element

d_i,d_0 inner and outer tube diameter, inches

d_c mean catalyst particle diameter, inches

F_0 feed rate of ethylbenzene, lb-mole/hr*tube

F_{EB} molar flow rates of ethylbenzene, lb-mole/hr*tube

F_{ST}, F_{H2} for styrene and hydrogen

U overall heat transfer coefficient, Btu/hr*ft^{2*0}F, based on do (assume constant)

H_{rl} standard heat of reaction at 77^{o}F for first reaction (Eq. 1), BTU/lb-mole,

H_{r2}, .H_{r3} for the other two reactions

P_o total pressure at reactor inlet, psia

P, pressure in reactor, psia

z axial distance from reactor inlet, ft

å void fraction in the tubes, ft3void/ft3 total volume

ρ_C catalyst density, lb catalyst/ft ^{3}reactor

ρ_p catalyst density, lb catalyst/ft^{3}catalyst

REFERENCES:

1. Wenner, R. R. and E. C. Dybdal, "Catalytic Dehydrogenation of Ethylbenzene, *Chem. Eng. Progr.*, **44**, 275 (1948).

2. Peters, M. W. and K. D. Timmerhaus, "Plant Design and Economics for Chemical Engineers", Fourth Edition, McGraw-Hill Book Company, New York, 1991.

3. Faith, W. L., D. B. Keyes, and R. L. Clark, *Industrial Chemicals*, Wiley & Sons, NY (1950).

4.H.Scott Fogler, " Elements of Chemical Reaction Engineering ", Third Edition, Printice-Hall of India, New Delhi, 1997

5. www.uop.com

6. http:// cheweb.tamu.edu