# CHAPTER 4

ENERGY CONSERVATION

Chapter (4)

Energy Conservation in Gas-to-Liquids Fischer –Tropsch Synthesis

Energy conservation has always been a targeted objective in the design and operation of chemical plants, GTL is not an exception. However, although the synthesis it self is an exothermic reaction, and steam is generated in many locations of the process as a byproduct, any savings in the feedstock (natural gas) is considered as energy saving. Means undertaken to achieve energy or gas conservation in the different manufacturing stages of the GTL process will be discussed.
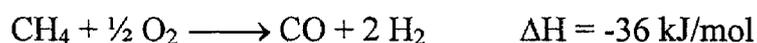
4-1-Energy conservation in the synthesis gas production stage:

Production of synthesis gas can be achieved by the following reactions:

Steam reforming,

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2 \qquad \Delta H = 206\ kJ/mol$$
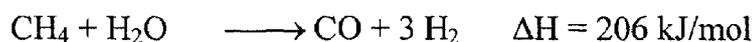
And partial oxidation,

$$CH_4 + \tfrac{1}{2}\ O_2 \longrightarrow CO + 2\ H_2 \qquad \Delta H = -36\ kJ/mol$$

The predominant commercial technology for syngas generation has been and continues to be, steam methane reforming, SMR, in which steam and methane are catalytically and endothermically converted to hydrogen and carbon monoxide. An alternative approach is partial oxidation, POX, the exothermic, non catalytic reaction of methane and oxygen to produce a syngas mixture. SMR and POX produce syngas with different compositions. In particular SMR produces a syngas having much higher H_2 / CO ratio which is an advantage in case of ammonia manufacture. However, neither SMR nor POX is ideally suited to GTL applications, where, H_2 / CO of about 2 is required. A solution to this dilemma is to use both technologies. For example POX and SMR can be used in parallel to produce syngas streams having different compositions, but, when mixed together they give the composition required by F-T synthesis. An alternative approach is autothermal

reforming, ATR, which combines partial oxidation with catalytic reforming in one reactor. The process is autothermal in that the endothermic reforming reactions proceed with the internal combustion (or oxidation) of portion of the feed hydrocarbons. ATR properly refers to a standalone single step process for feedstock conversion to syngas. The fluidized bed autothermal reactor developed by Exxonmobil for the AGC-21 GTL process **figure (4-1)** is an example. The ATR process may be equivalently referred to a two stage process where natural gas is partially steam reformed in a gas heated primary reformer and then partially oxidized with oxygen in an autothermic reformer. The heat generated in the secondary reformer is carried by the raw syngas to heat the primary reformer. Examples are the ICI combined reforming process **figure (4-2) [Abbot, 1998]** and Lurgi combined reforming **figure (4-3) [Higman, 1990]**. The row syngas leaving the primary reformer at around 975°C still contains sensible heat enough to generate high pressure steam and law pressure steam before it cools. Autotermal reforming is an elegant way to achieve energy conservation and at the same time get the synthesis gas composition required by the F-T process.

4-2-Energy conservation via process integration:

As mentioned above high pressure steam and low pressure steam which can be used as process steam and for power generation are generated in the synthesis gas production section. Fischer–Tropsch reaction is also highly exothermic and the heat generated in the F-T reactor is utilized for the production of high, intermediate and low pressure steam which can be utilized in the process or directed to electricity generation. However, substantial quantities of gaseous hydrocarbons including methane are produced. In principle it is desirable to recycle these gases to produce more synthesis gas. On the other hand it is necessary to provide a purge for inerts (argon and nitrogen) from the loop. Also it is requested that a side stream be allocated for hydrogen production as hydrogen is needed for hydrocracking of the produced heavy wax in the product upgrading section. The block diagram **(figure 4-3)** of Lurgi shows how these considerations are met in a combined reforming for F-T synthesis. The F-T tail gas is recycled to the second reformer. The fuel demand in the primary reformer acts as a purge stream to keep inerts within acceptable limits

the loop. The feed to PSA for hydrogen production is taken off the outlet of CO_2 removal unit.

Handling of these issues is different in synthesis gas based unit where there is no primary reformer [Higman, 1990]. The outlet of the inert is a separate hydrogen manufacturing unit with its own reformer, using tail gas as the process feed and fuel figure (4-4). The fuel gas stream for steam boilers or refinery heaters is a possible alternative.
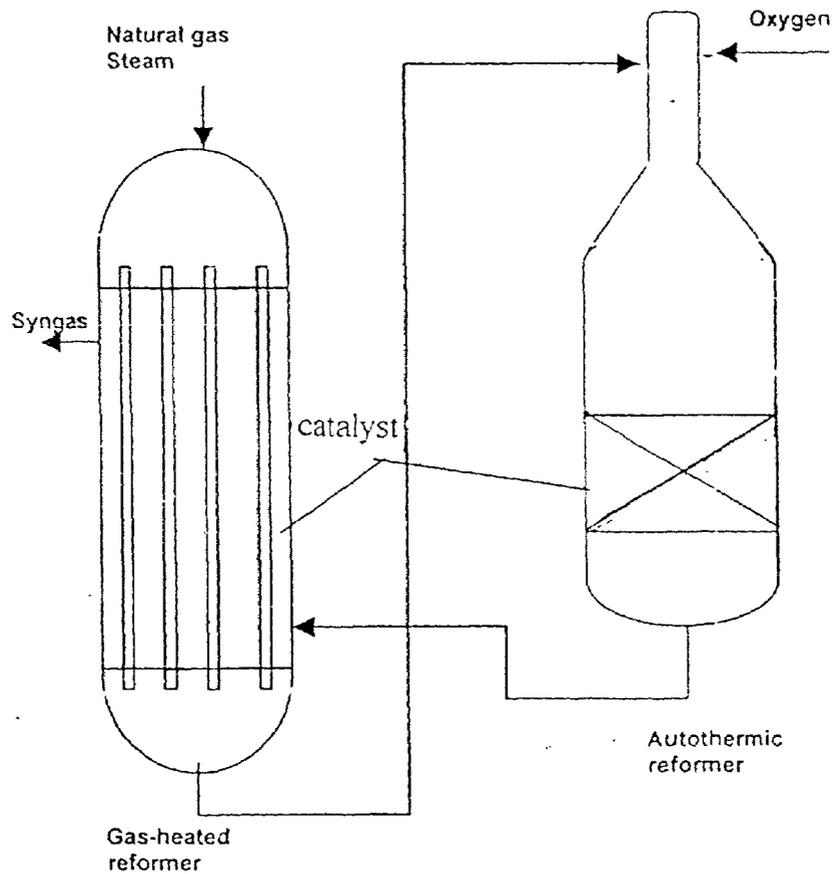

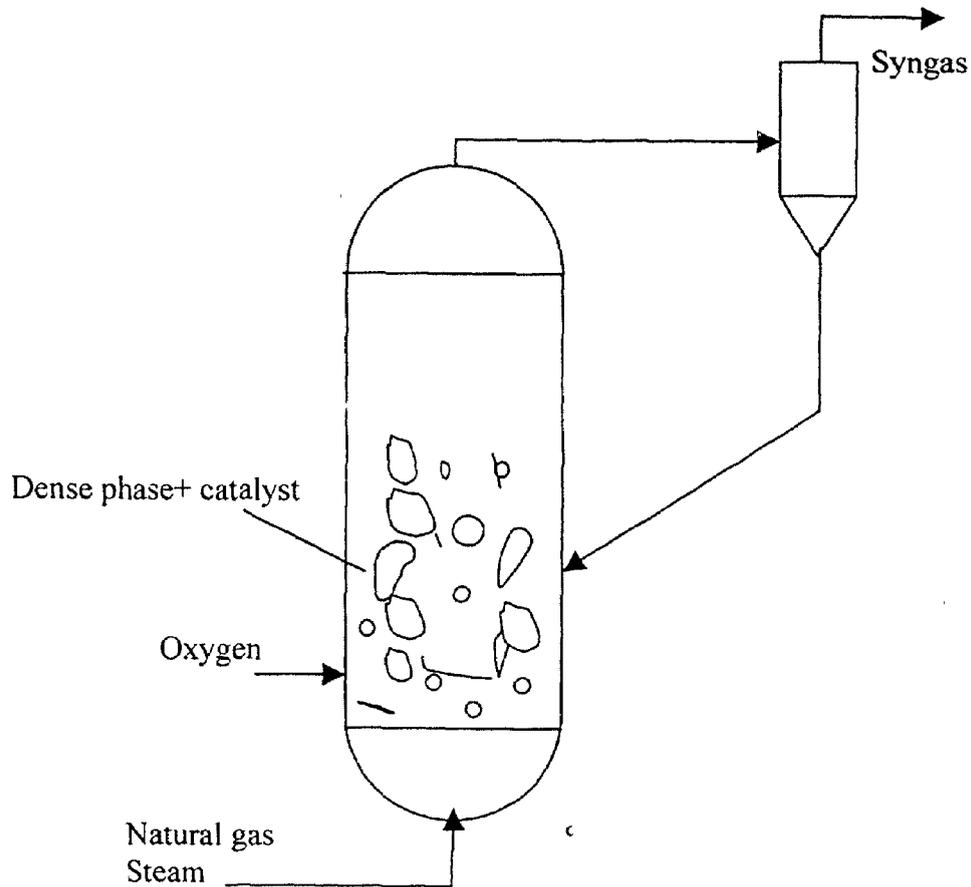figure (4-1) ICI Combined- Reforming

figure (4-2) Combined autothermic- reformer (Exxon CAR)

4-3- Maximizing power generation:

Maximizing power generation is another approach to make use of unconverted F.T out gases, other than recycling them to the F-T slurry reactor, or to synthesis gas generation section. The produced power may be sold so as to add to the products revenue and therefore improves the process economics. **Choi et al. [1997]** performed a process simulation study for a once through natural gas F-T plant with power co-production. The plant was designed to process 100 MMSCF/day natural gas and produce roughly 8,820 BPD of F-T syncrude and 84 Mw of export power. **Figure [4-5]** is a simplified block flow diagram showing the process configuration of the synthesis section. Area 100 is dedicated for synthesis gas generation and area 200, for once-through F-T synthesis and product fractionation.

Synthesis gas area (100) consists of the 3 major plants; air compression and separation, autothermal reforming ATR and CO_2 removal and recycle. This area produces nitrogen -diluted synthesis gas with H_2/CO molar ratio of 2. Sulfur is recovered from natural gas by adsorption on ZnO. Optimization studies showed that ATR with 40% enriched air with CO_2 recycle was the best choice.

Fischer-Tropsch synthesis and product formation area (200) consists of 4 plants, once through F-T synthesis, product separation, hydrogen recovery plant and wax hydrocracking. A small hydrogen recovery plant (PSA) is to recover enough hydrogen for hydrocracking. The PSA feed is taken from the synthesis gas stream entering F-T reactor. F-T synthesis is performed in two stages with a total conversion of 85%. Excess heat is removed by generation of 150 psig steam from tubes within the F-T reactor. The plant uses all the byproduct steam and fuel gas to supply its internal electric power and heating requirements. In addition it produces about 84 Mw of exported electric power. Power production is achieved in the combined cycle plant shown in **figure (4-6)**. It has been found that the plant economics is highly dependent on the power selling price.
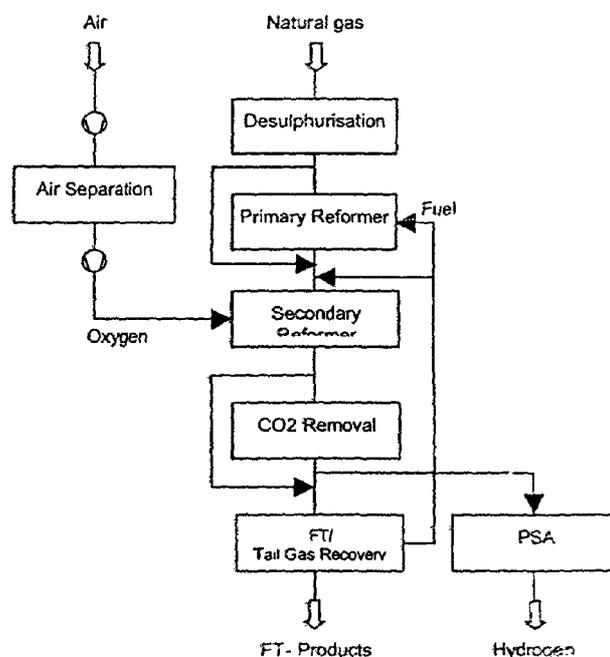

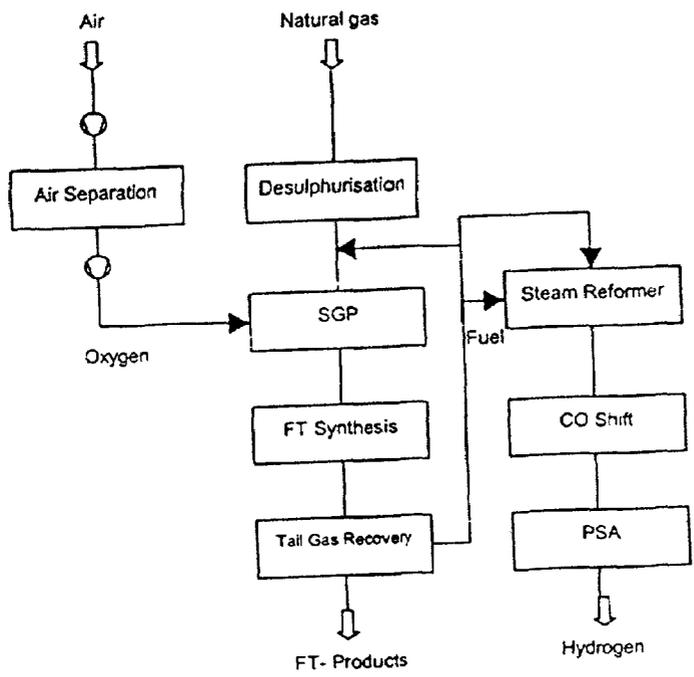Figure 4-3 Lurgi Combined Reforming for F-T Synthesis
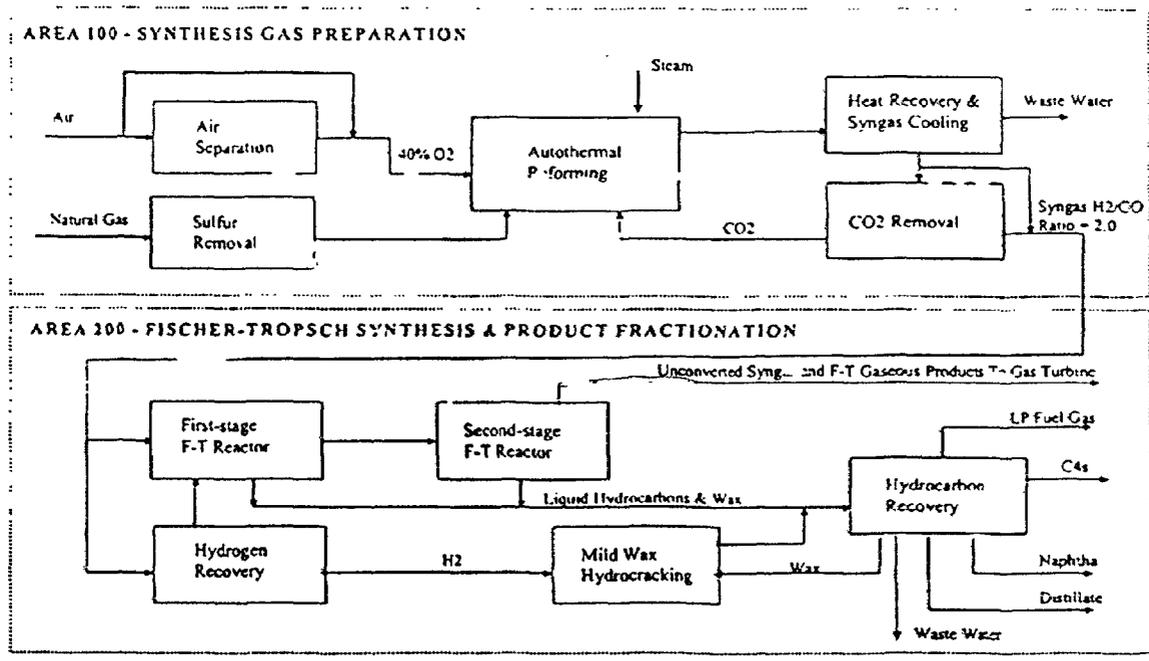
Figure 4-4 SGP for F-T Synthesis

Figure 4-5 Once-Through Fischer-Tropsch (F-T) Design with Power Co-Production (Overall Process Configuration)
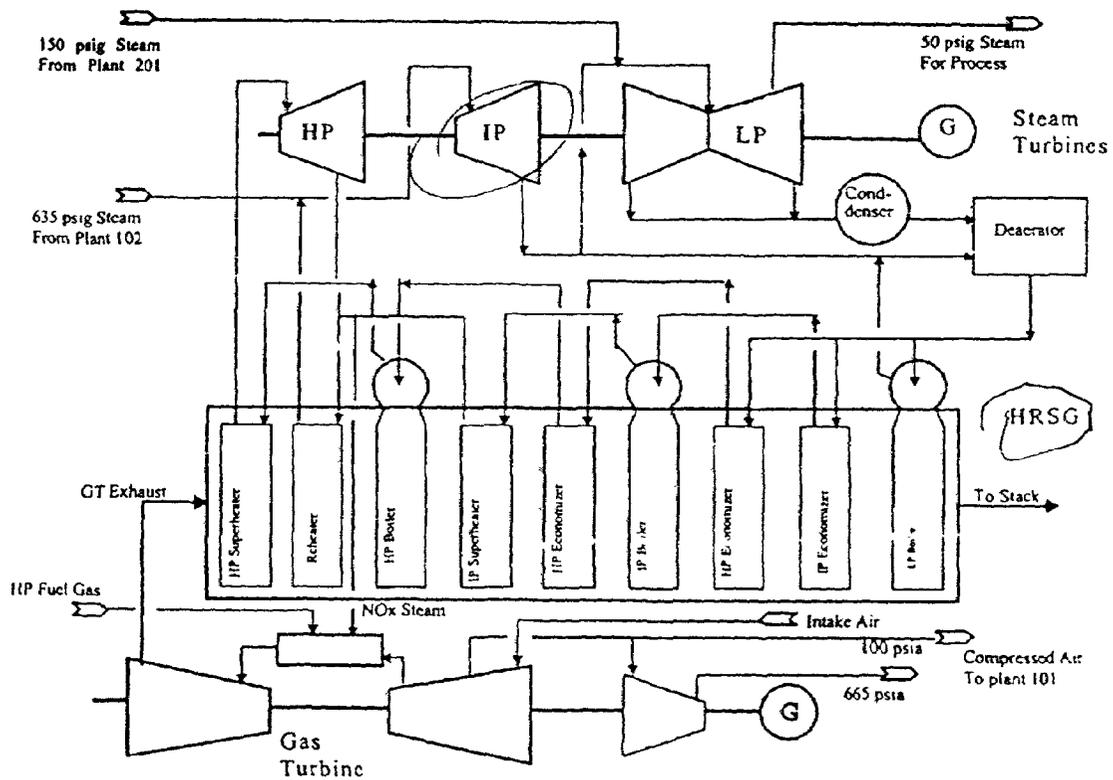
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Figure 4-6 Block Flow Diagram - Combined Cycle Plant

4-4-Energy conservation in Fischer Tropsch synthesis section through optimum design of the heat exchanger network

Typically, 20- 40 % energy saving, coupled with capital savings, could be realized in state of the art flow sheets by improved Heat Exchanger Networks (HENs) design. The objective of Heat Exchanger Network Synthesis (HENS) is to maximize exchange of heat between hot streams (streams required to cool from their supply temperatures to their target temperatures) and cold streams (streams required to heat from their supply temperatures to their target temperatures) using heat exchangers. The Maximum Energy Recovery (MER) network minimizes the utility usage. An optimization procedure is proposed by which trade-offs between

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utility savings and added investment cost are taken into account to design an optimum **HEN**. The total heat transfer area and the number of units of the **HEN** represent the most important factors in determining capital cost. The temperature difference between hot side and cold side of every heat exchanging match ΔT_{min} is an important factor which affects both operating and capital cost **[Hohmann, 1971]**, **[Umeda et al. 1979 a,b]**, **[Nishida et al. 1981]**, **[Townsend and Linnhoff 1984]**, **[Saboo et al. 1986 a,b]**, **[Ahmad and Linnhoff 1984]**, **[Zhu et al. 1995a,b]** and **[Lewin et al. 1998a,b]** and **[Galli and Cerda1998a,b]**.

4-4-1-Design of Heat Exchangers Networks (HEN):

The design objective includes a quantitative part (targeting of utilities and cost of heat exchange equipment) and a qualitative part (safety , operability, flexibility, controllability).Research is progressing along three different lines which are the use of thermodynamic concepts, mathematical methods, and the use of knowledge based systems for process design. In order to solve real life industrial problems, the engineer should take advantage of all these disciplines. However, the skill and experience of the engineer himself will remain of vital importance.

Steps of **HENS** Design

1- Targeting of operation cost by prediction of minimum utilities.

2- Targeting of capital cost by minimization of the heat transfer area.

3- Design of the heat exchangers network **(HEN)**.

4- Improve and develop of **HEN** design in order to reach the optimum or nearly optimum condition of minimum operating and capital cost.

4-4-1-1 AMU Program for Prediction of Minimum Utilities:

The software program [Automatic prediction of Minimum hot and cold Utilities (**AMU**) has been developed in the Egyptian Petroleum Research Institute [EPRI] by the designers' teamwork. This program automatically formulates the transshipment model of **Papoulias and Grossmann [1983]** for minimum utilities requirement in a form that can be read by mathematical optimization software [**LINDO**]. The required data are the conditions of the streams, inlet and target temperatures and heat capacity flow rates and ΔT_{min} .When the program **AMU** has

written the formulation to a file then **LINDO** is applied to solve the transshipment model giving the minimum hot and cold utilities.

Theoretical algorithm of AMU:

The first step in finding the minimum utilities is to partition the entire temperatures range for all streams into K temperatures intervals; the interval boundary temperatures are set according to input streams temperatures with keeping the hot boundary temperature higher than the cold boundary temperature by ΔT_{min}. Heat balance around each interval is taking place as shown in **figure (4-7A)**. The formulation depends on the maximization of the use of heat in all hot streams in all intervals. **Figure (4-.7B)** shows the flow diagram of AMU program

IF Q_{ik} is the heat available in hot stream i entering temperature interval k then:

$$Q_{ik} = F_i (Cp)_{ik} \Delta T_k^i$$

IF Q_{jk} is the heat load flowing to cold stream j from temperature interval k then:

$$Q_{jk} = F_j (Cp)_{jk} \Delta T_k^j$$

The heat load of a hot utility m in the temperature interval k is given by:

$$QH_k = F_m^s \Delta H_{mk}$$

Similarly, the heat load of cold utility n in the temperature interval k is given by:

$$QC_k = f_n^w \Delta H_{nk}$$

Defining R_k as the residual heat flowing out of interval k then transshipment model for minimum utility is given by the model of **Papoulias and Grossmann [1983]** equation (4-1):

Minimize $$Z = \sum_{k=1}^{K} QH_k + \sum_{k=1}^{K} QC_k \qquad (4-1)$$

Subject To:

$$R_k - R_{k-1} - \sum_k QH_k + \sum_k QC_k = \sum_{i \in H_k} Q_{ik} - \sum_{j \in C_k} Q_{jk}$$

k = 1, 2, ...K

$$F_m^s \geq 0 \qquad m \in s \qquad F_n^w \geq 0 \qquad n \in w$$

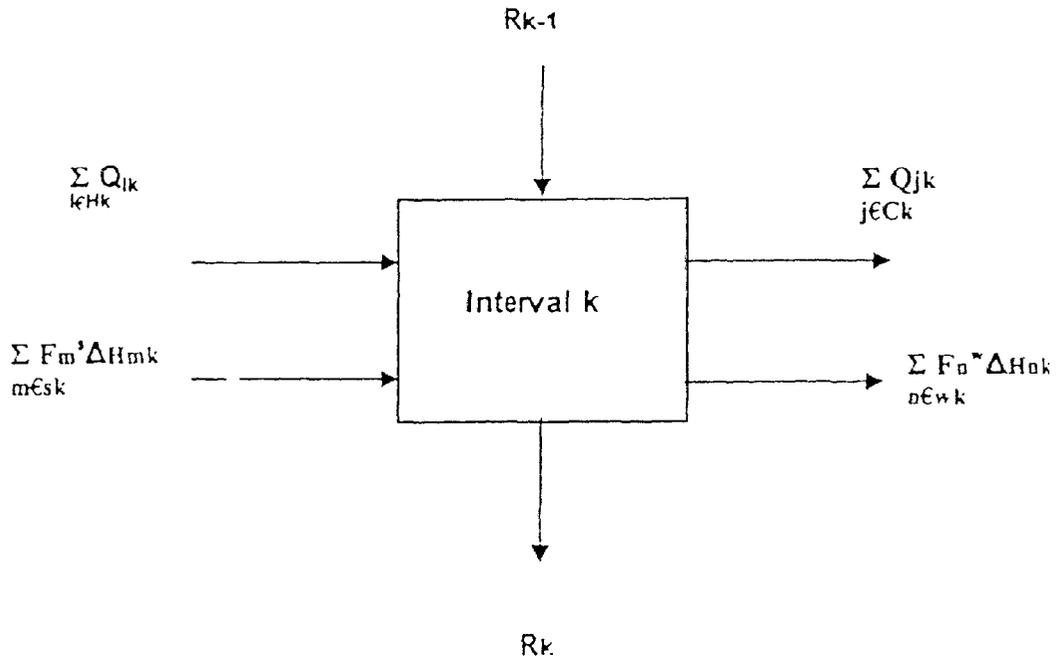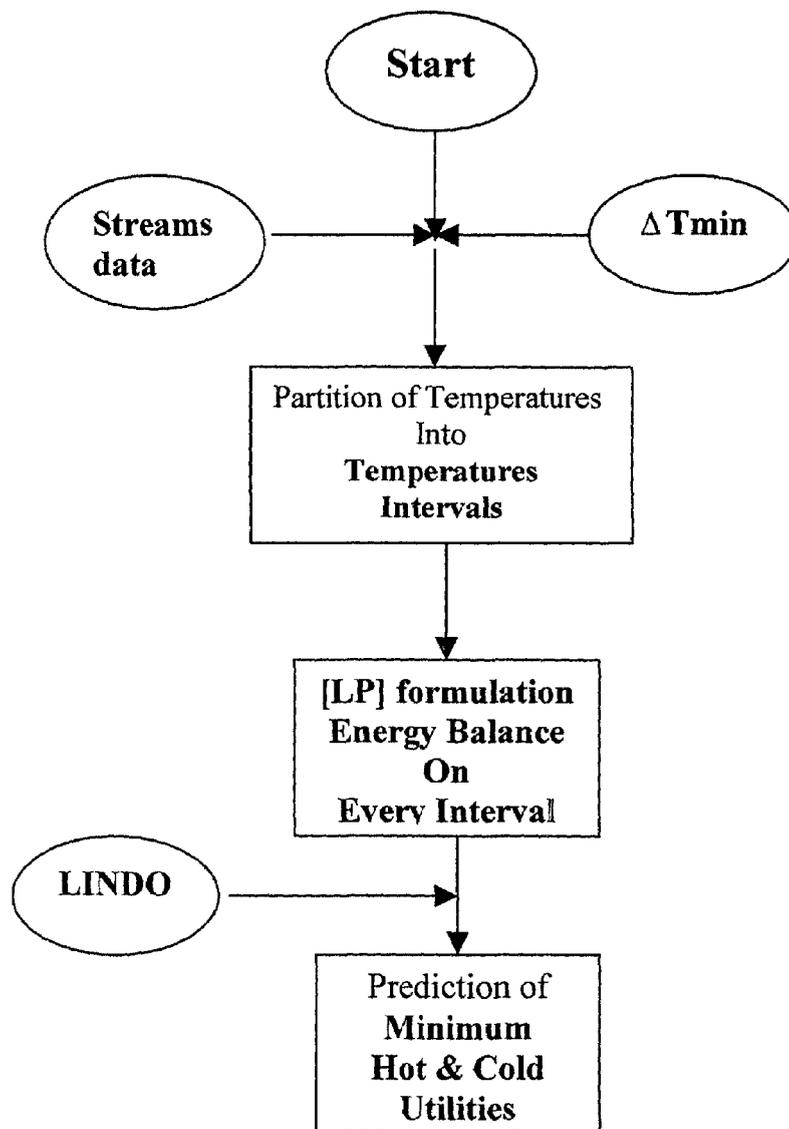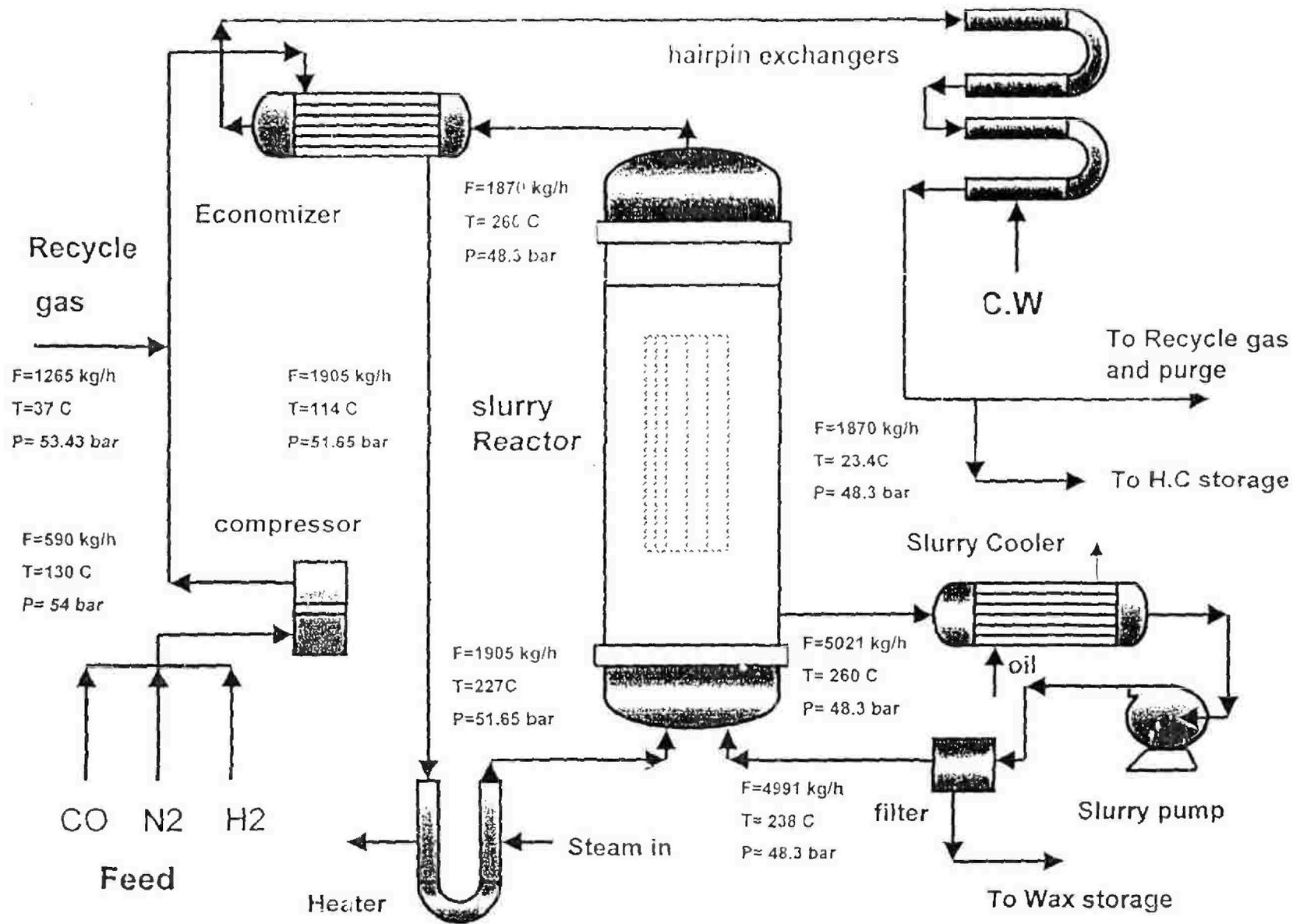$$R_0 = R_K = 0 \qquad R_k \geq 0 \qquad\qquad k = 1, 2, .K\text{-}1$$

Figure (4-7A) Heat flow pattern in each temperature interval

```
                    ┌─────────┐
                    │  Start  │
                    └────┬────┘
                         │
    ┌─────────┐          │          ┌─────────┐
    │ Streams │──────────┼──────────│ Δ Tmin  │
    │  data   │          │          └─────────┘
    └─────────┘          ▼
              ┌────────────────────────┐
              │  Partition of Temperatures │
              │          Into          │
              │      Temperatures      │
              │        Intervals       │
              └───────────┬────────────┘
                          │
                          ▼
              ┌────────────────────────┐
              │   [LP] formulation     │
              │    Energy Balance      │
              │          On            │
              │      Every Interval    │
              └────────────────────────┘
    ┌─────────┐                │
    │  LINDO  │────────────────┤
    └─────────┘                ▼
              ┌────────────────────────┐
              │     Prediction of      │
              │       Minimum          │
              │      Hot & Cold        │
              │       Utilities        │
              └────────────────────────┘
```

Figure (4-.7B) Flow Diagram of AMU Program

Since process flowsheets for F-T synthesis available in the open literature contains no detailed stream data, the stream data of the demonstration AFDU Fischer-Tropsch pilot unit described in chapter 3 was considered for analysis. Of course the same results reached with the pilot scale unit can be applied to the industrial scale unit taking into consideration the scale factor. A full description of the demonstration unit, the hot streams and the cold streams are given in section (3-2-1) chapter 3. A simplified flow diagram is given in **figure (3-7C)**. Table (4-1) show the streams data for the AFDU pilot unit.

hairpin exchangers

Economizer

Recycle

gas

F=1265 kg/h
T=37 C
P= 53.43 bar

F=1905 kg/h
T=114 C
P=51.65 bar

F=187(kg/h
T= 26(C
P=48.3 bar

slurry
Reactor

C.W

To Recycle gas
and purge

F=1870 kg/h
T= 23.4C
P= 48.3 bar

To H.C storage

compressor

F=590 kg/h
T=130 C
P= 54 bar

Slurry Cooler

oil

F=1905 kg/h
T=227C
P=51.65 bar

F=5021 kg/h
T= 260 C
P= 48.3 bar

CO   N2   H2

Feed

Heater

Steam in

F=4991 kg/h
T≈ 238 C
P≈ 48.3 bar

filter

Slurry pump

To Wax storage

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Fig(7-c) Simplified flow diagram for the AFDU pilot unit

Table [4-1]: Streams Data of Fischer-Tropsch Process

Stream No.	Tin °C	Tout °C	Heat capacity flowrate MJ/h°C	Heat transfer coeff. MJ/h m^2°C
Reactor Inlet C1	100.5	227	3.913	3.579
Reactor Product h2	260	23.4	3.482	3.600
Slurry	260	239	12.774	5.28
Hot utility h1	300	299	0.0	0.18
Cold utility C2	15	25	0.0	0.72

The Grid Diagram

The heat exchanger network is best represented by the grid diagram developed by **Linnhoff et al [1982]**. In the grid diagram hot streams are represented by straight lines starting from the left-hand-side and stretching to the right, while cold streams are represented by straight lines starting from the right-hand-side and stretching to the left. Heat exchangers are represented by circles on the exchanging streams connected by a vertical line. Heaters and coolers are represented by circles on their respective streams. The grid diagram of the existing heat exchanger network is given in **figure (4-8)**.
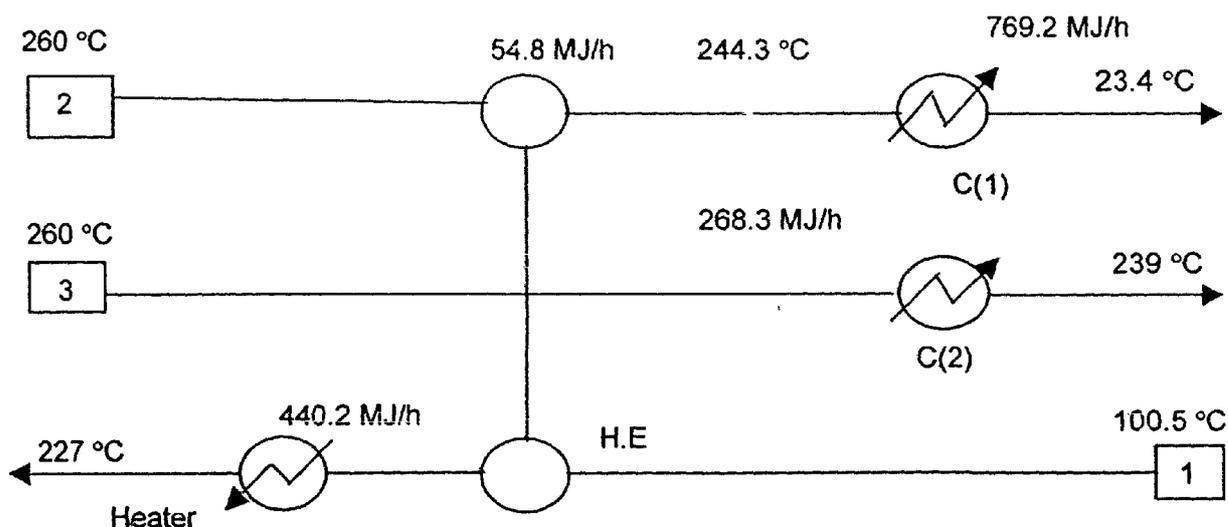

Figure (4-8) Actual gride diagram for the existing heat exchangers network of liquid phase Fischer-Tropsch QH = 440.2 MJ / h and QC = 1037.5 MJ / h

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The (AMU) program has been applied on the Fisher-Tropsch process (using the data of table [4-1] at different values of ΔTmin namely ΔTmin = 10, 20, 30, 40, and 50 °C. The first step, (AMU) program automatically formulates and writes the energy balance equations of the process streams in a file. The second step, LINDO solves the equations to predict minimum hot and cold utilities at the defined ΔTmin. Finally, design of the HEN with minimum utilities, at the defined ΔTmin, can take place namely using the grid diagram. A typical output (heat balance equations) for the (AMU) program and the solution by LINDO at ΔTmin = 10 °C are given below:

Design of HEN at ΔTmin of 10 °C:
Energy Balance Equations at ΔTmin of 10 °C as written by (AMU) program:

```
MIN QH + QC
SUBJECT TO
R1-R0 + QC1 - QH1=      .00
R2-R1 + QC2 - QH2=   293.82
R3-R2 + QC3 - QH3=   297.71
R4-R3 + QC4 - QH4=     5.57
QH -QH1 -QH2 -QH3 -QH4 =0.0
QC -QC1 -QC2 -QC3 -QC4 =0.0
R0=0.0
R4=0.0
END
```
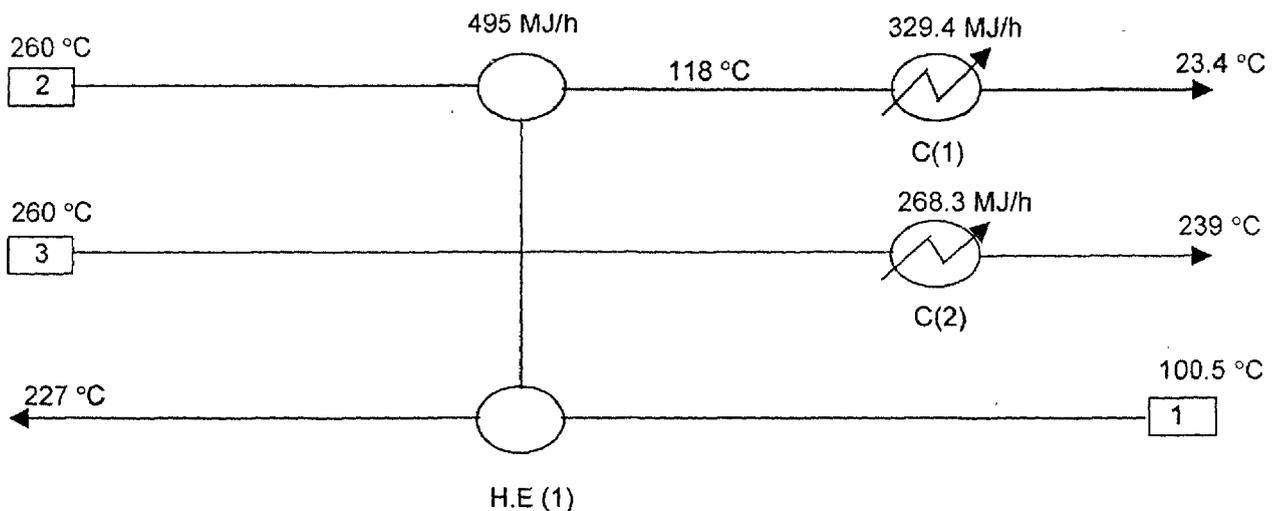

Figure 4-9 Heat Exchangers Network of Liquid Phase Fischer-Tropsch
$(Q_H = 0.0, Q_C = 597.1$ MJ/h, Area = 17.8 m, No=3 at ΔTmin = 10)

LINDO optimum solution

LP OPTIMUM FOUND AT STEP   4

OBJECTIVE FUNCTION VALUE   1)   597.1000

VARIABLE	VALUE	REDUCED COST
QH	0.000000	0.000000
QC	597.099976	0.000000
R1	0.000000	2.000000
R0	0.000000	0.000000
QC1	0.000000	2.000000
QH1	0.000000	0.000000
R2	0.000000	0.000000
QC2	293.820007	0.000000
QH2	0.000000	2.000000
R3	0.000000	0.000000
QC3	297.709991	0.000000
QH3	0.000000	2.000000
R4	0.000000	0.000000
QC4	5.570000	0.000000
QH4	0.000000	2.000000

It is clear from **LINDO** solution that the value of the objective function i.e $QH + QC = 597.1$ Mj at the same time the hot utility $QH = 0$ i.e there is no need for hot utility at all. Hence all 597.1 go to the cold utility. The **HEN** for the above results is deduced manually and shown in **figure (4-9)**.

The same procedure was repeated for the other $\Delta Tmin$ values. The corresponding **HEN** was deduced for each case as given in **figures (4-10 to 4-13)**. We notice that the hot utility started to appear at $\Delta Tmin = 40$ °C. To find the minimum cost heat exchanger network, the area of exchangers + coolers + heaters was calculated for each unit from equation (4-2):

$$A = \frac{Q}{U} \frac{1}{\Delta T_{lm}}$$ (4-2)

where U is the overall heat transfer coefficient given by:

$$U = \frac{1}{h_1} + \frac{1}{h_2}$$

and Q is the heat load assigned to the specific exchanger. The number of units and the total area requirements are given in table (4-2).

Table [4-2] Economic Analysis of the HEN Designs of Fischer-Tropsch at different values of ΔTmin:

| ΔTmin Network Details	10°C	20°C	30 °C	40°C	50°C
Target hot utility MJ/h	0.0	0.0	0.0	27.8	66.5
Target cold utility MJ/h	597.1	597.5	596.4	624.5	663.4
% Saving of hot utility	100%	100%	100%	93.7%	84.9%
% Saving of cold utility	42.4%	42.4%	42.4%	39.8%	36.1%
No of Units	3	4	4	5	5
Heat transfer area m^2	17.8	16.83	14.44	14.84	16.13
Cost of Utility saved $/yr	18158.2	18158.2	18158.2	17012.3	15415.5
Ann. Capital Cost $/yr	17574.2	22861.9	22732.2	28335.2	28217.0
Ann. Operating Cost $/yr	1188.4	1188.4	1188.4	2233.1	3929.8
Ann. Overall Cost $/yr	18762.5	24050.3	23920.63	30568.3	32146.8
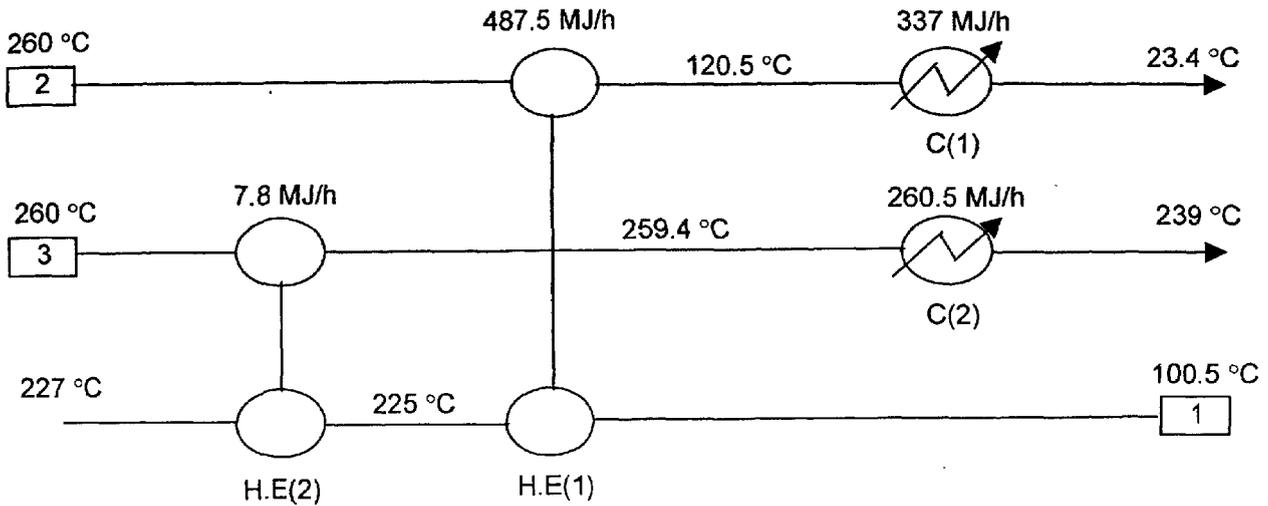
Figure (4- 10) Heat Exchangers Network of Liquid Phase Fischer-Tropsch

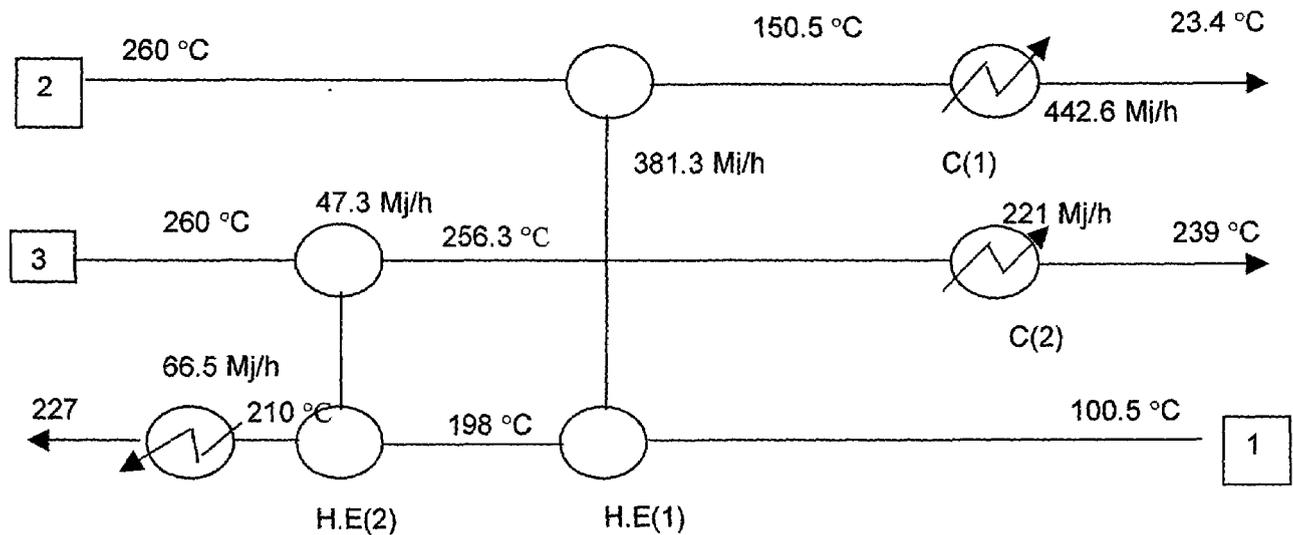$(Q_H = 0.0, Q_C = 596.4$ MJ/h, Area=16.83 m, NO = 4 at $\Delta Tmin = 20$ °C)
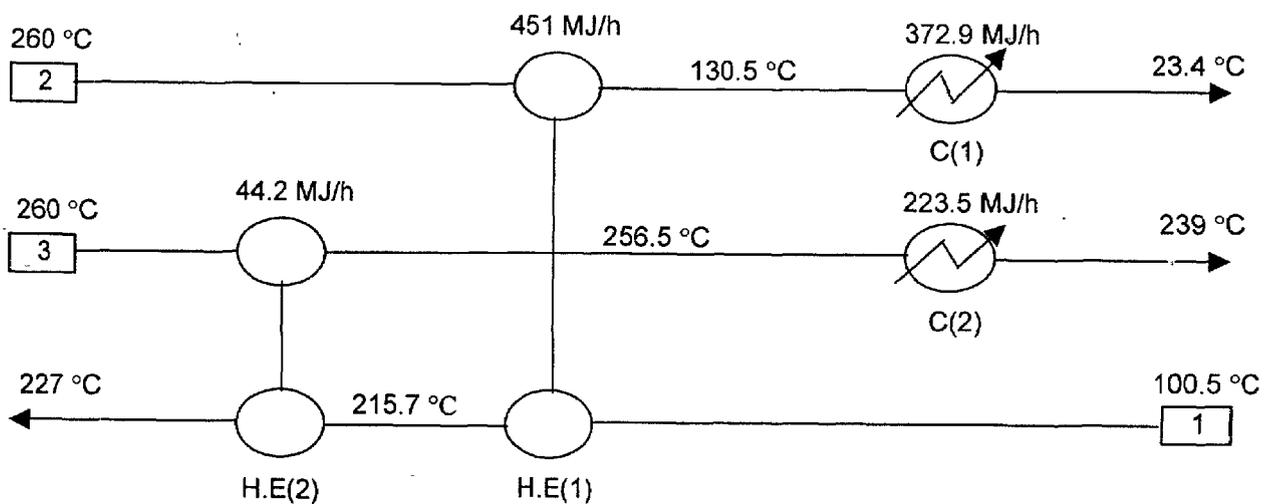
Figure (4- 11) Heat Exchangers Network of Liquid Phase Fischer-Tropsch

$(Q_H = 0.0, Q_C = 597.5$ MJ/h, Area=14.44 m, NO = 4 at $\Delta Tmin = 30$ °C)

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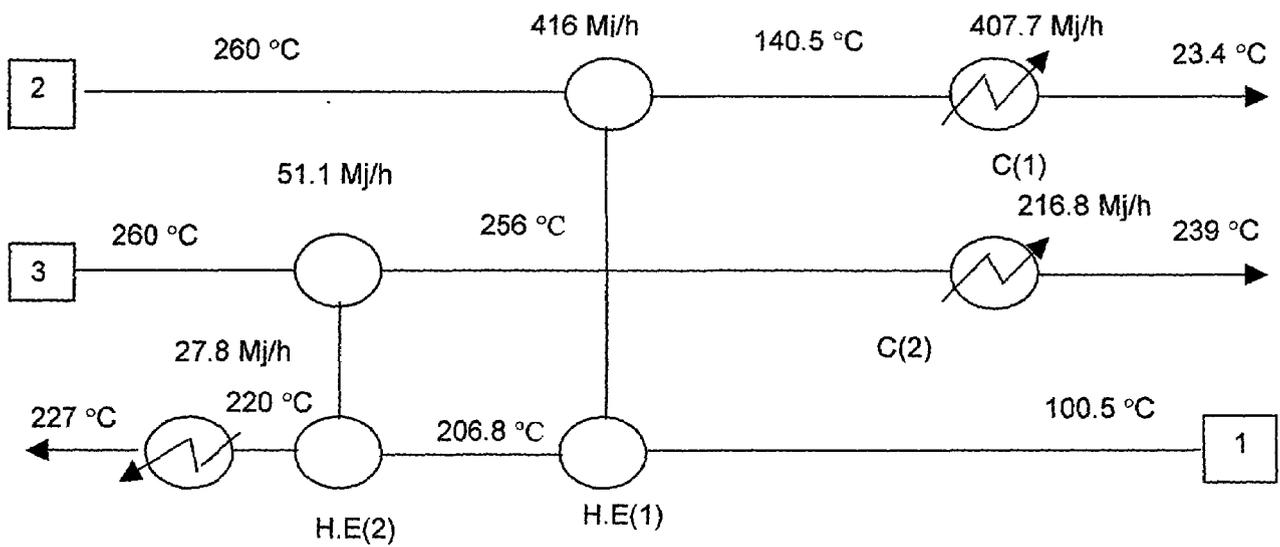
Figure (4- 12) Heat Exchangers Network of Liquid Phase Fischer-Tropsch

$(Q_H = 27.8, Q_C = 624.5$ MJ/h, Area=14.84 m, NO = 5 at ΔTmin = 40 °C)

Figure (4- 13) Heat Exchangers Network of Liquid Phase Fischer-Tropsch

$(Q_H = 66.5$ Mj/h, $Q_C = 663.4$ MJ/h, Area=16.13 m, NO = 5 at ΔTmin = 50 °C)

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Annualized Overall Cost

The cost of HEN in each case is calculated as the annualized overall cost as follows:

Annualized Overall Cost of HEN = Annualized capital cost + Utilities cost

Annualized capital cost = [$\sum$Actual cost of unit& coolers + $\sum$Actual cost of heaters] /L.f (life time)

Cost of a unit = 30800 + 750 (A^0.81) ... For H.E or cooler [ZHU et al. 1995]

L.f (Life time of the plant) = 6 years [ZHU et al. 1995]

- Annual Cost Index of Chemical Eng. Plant (C.I) as:

$C.I_{2003}$ = 395.6, $C.I_{1995}$ = 381.1, $C.I_{1979}$ = 230   [Chem.Engng journal, April 2003]

Actual cost of unit = Cost of unit x [$C.I_{2003}$ / $C.I_{1995}$]

Actual cost of heater=Cost of heater[$C.I_{2003}$ /$C.I_{1979}$][Peters and Timmerhaus, 1981].

According to the recent Egyptian prices of utilities:

Cost of hot Utility = 140.2 $/ (kW/yr) and Cost of cold Utility = 7.1 $/ (kW/yr)

Table (4-2) summarizes the results obtained at different minimum approach temperatures $\Delta Tmin$ it is noticed that the same zero hot utility was obtained for $\Delta Tmin$ =10, 20 and 30 °C, also the same cold utility of 597.1 MJ was needed for these cases. As $\Delta Tmin$ increases to 40 and 50 °C hot utility is observed to increase and so does the cold utility. The increase in hot utility is being compensated for by a similar increase in cold utility. More heat in = more heat out, this one future of the pinch analysis [Linnhoff , 1982]. Table (4-2) also shows the amount of saving in each of the hot and cold utilities above the based case. A maximum of 100% savings in hot utility and 42.4 % savings in cold utility could be achieved for the $\Delta Tmin$ = 10, 20 and 30 °C. The minimum number of units is 3. This is achieved only at $\Delta Tmin$ = 10 °C.

Finally the cost data shows that the minimum overall cost corresponds to $\Delta Tmin$ = 10 °C. At $\Delta Tmin$ = 10 °C we get minimum hot and cold utility, hence minimum operating cost. Minimum number of units through not minimum area, but minimum overall capital cost.

By studying these results we can define that, the optimum value of ΔTmin is 10°C which can realize the optimum design of HEN with minimum number of units, minimum consumed utilities, minimum operating cost, minimum capital cost and so on the minimum overall cost could be achieved.

Power production

The heat generated in the slurry bubble column as a result of the highly exothermic Fischer-Tropsch reaction is usually used to generate steam which can then be used in the plant or directed to electric power generation.

In the present case the pilot AFDU unit for case (AF-R16-1B) the reported heat generated from F-T reaction is equivalent to 667.6 kW (see Appendix C). Assuming a conversion efficiency of heat to electricity of 35%, then the power generated would be equal to 233.7 kW.

The synthesis gas feed rate to this unit = 35.36 kmol/h. an industrial scale unit producing one million t/y middle distillates would require synthesis gas feed of 27861 k mol/h [Higman, 1990]. The electric power generated from such a unit would be equal to 27861 x 233.7/35.36= 184 Mega Watt.