CHAPTER III

PROCESS SELECTION

The natural gas in the Gulf of Thailand will be transmitted through pipelines starting 1982. The composition of the gas mixture at the well head is shown in Table III-1.

Table III-1

Gas Composition of the Natural Gas from

the Gulf of Thailand

Methane	66 – 80 %
Ethane	10 – 7 %
Propane	5 – 3 %
Butane & Hexane	3 – 1 %
Nitrogen	1 – 0.1%
Carbon Dioxide	13 – 7.9%

Source: Petroleum Authority of Thailand

As there is a little portion of hydrogen sulfide which is rather corrosive to the pipelines, the hydrogen sulfide is scrubbed at the platform. The composition through the pipelines is as above. Carbon dioxide is not so corrosive, and is transmitted with the natural gas through pipelines.

However, carbon dioxide is an undesired product containing in the natural gas, it is to be scrubbed at the receiving station onshore. Also

butane, propane, hexane, pentane and ethane are of industrial values, the extraction and separation of all these are desired to purify the gas and to divert these hydrocarbons to a more worthwhile use, and also, to concentrate methane. The gas composition after the receiving station onshore is calculable, but is typically composed of methane. The typical composition of the natural gas to be used in industrial sectors is shown in Table II-1.

The natural gas gets into the process of the ammonia manufacturing process through these units:

1. Desulfurisation

2. Primary Reformer

3. Secondary Reformer

4. High-temperature Shift Converter

5. Low-temperature Shift Converter

6. Carbon Dioxide Removal (Scrubbing)

7. Final Gas Purification (Methanation)

8. Ammonia Synthesis

9. Ammonia Storage.

In the above units, there are many reactions in each of them. The design equation for the reaction in each unit will be assumed roughly comprising of 1 basic reaction as:

1. The basic reaction for steam reforming is

$$CH_4 + H_2O \: ----- \: CO + 3 H_2$$

2. The basic reaction for CO shift conversion is

$$CO \quad + \quad H_2O \quad ----- \quad CO_2 \quad + \quad H_2$$

3. The reaction for the synthesis conversion is

$$N_2 \quad + \quad 3 H_2 \quad ----- \quad 2 NH_3$$

The ammonia plant process diagram is shown in figure III-1.

3.1 Desulfurisation

Natural gas enters the process through a compressor at a pressure of 500 psig. It is assumed that the natural gas feed pressure is 100 psig. However pure the gas is, it is still required to purify the gas from sulfur compounds, for these compounds deactivate the 6 catalysts in the process, namely, primary reformer catalyst, secondary reformer catalyst, high-temperature shift converter catalysts, low-temperature shift converter catalyst, the methanation catalyst and the synthesis catalyst, especially the poisoning of the Ni-catalyst in the primary reformer and depositing of carbon on the catalyst must be prevented. This desulfurisation is used to safeguard the catalysts.

The natural gas at 500 psig and ambient temperature is passed through the activated carbon bed. Sulfur compounds are absorbed on the carbon or reacted with the metallic oxide in the carbon to form a metallic sulfide:
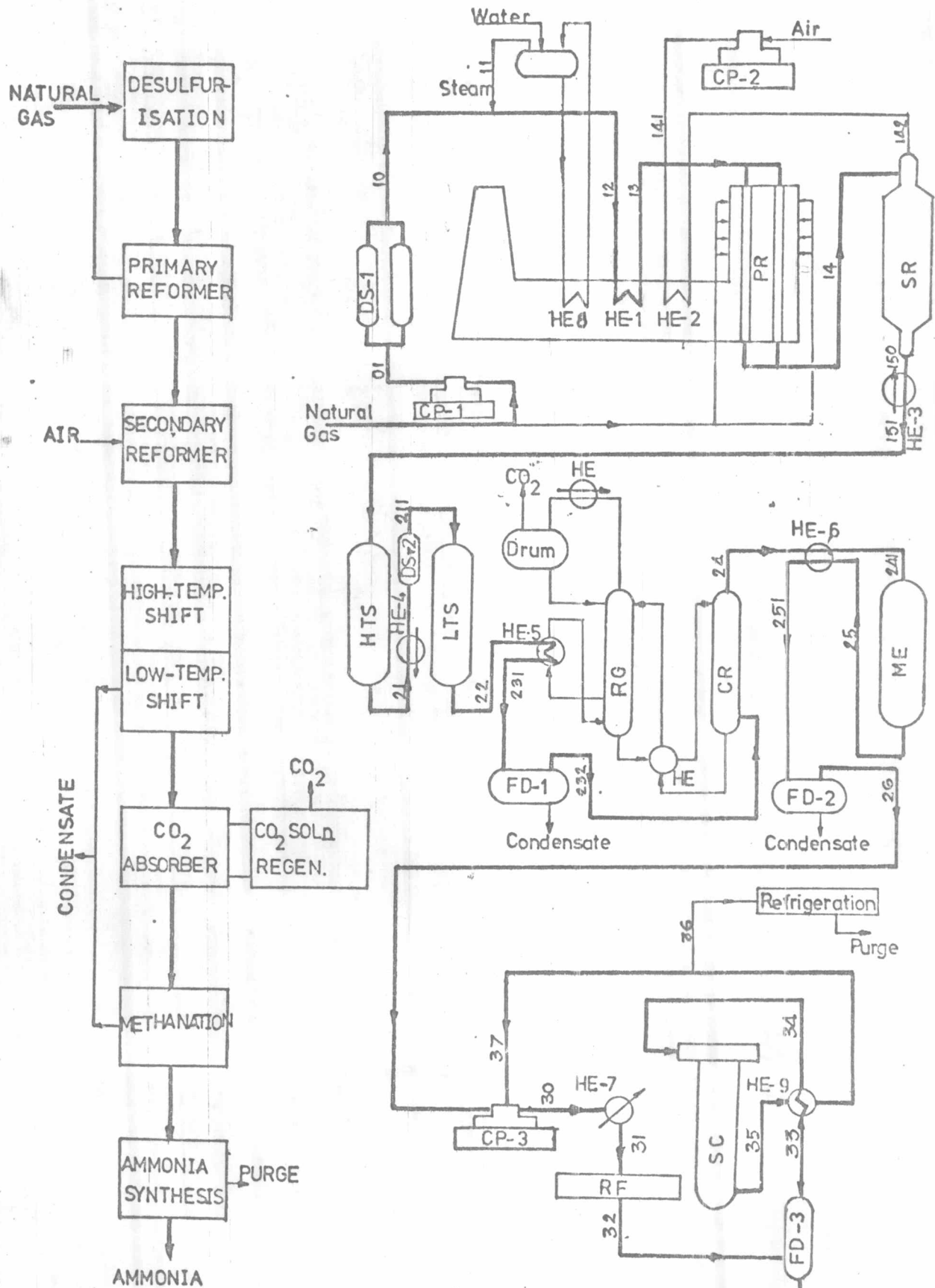
$$CuO \quad + \quad H_2S \quad --------- \quad CuS \quad + \quad H_2O$$

FIGURE III-1   Ammonia Plant Process Diagram

When the carbon bed becomes loaded with sulfur compounds, it is regenerated with steam or a mixture of steam and air at 400-450°F for several hours. The carbon bed is designed to be regenerated every 4-5 days. Two beds are designed to work; one being regenerated, another being in service. The free oxygen reacts with the metal sulfide to form the corresponding metal oxides and free sulfur which remains trapped in the carbon bed pores. Much of the sulfur is vented to the atmosphere along with the steam during regeneration.

3.2   Primary Reforming

After the desulfurisation, the natural gas is mixed with steam at a ratio of 3.5 and is heated to 930-1,020 °F in a waste heat recovery coil before the reaction in the primary reformer. The steam-carbon ratio is one factor to regulate the carbon deposition on the catalyst. High ratio will prevent the carbon deposition and also supplies steam for the CO shift conversion. Low ratio will encourage carbon deposition in the catalyst, endangering the catalyst.

In the reformer, catalyst composing of Ni-base as a major component is used to boost the reaction of the methane-steam formation. The reactions are as follows:

$$CH_4 + 2 H_2O \ ----- \ CO_2 + 4 H_2 \quad (\Delta H = - 39.5 \ kcal)$$
$$CH_4 + H_2O \ ----- \ CO + 3 H_2 \quad (\Delta H = - 49.3 \ kcal)$$
$$CH_4 + CO_2 \ ----- \ 2CO + 2 H_2 \quad (\Delta H = - 59.1 \ kcal).$$

The first and the second reactions are the major reactions of this unit. As they are endothermic reactions, heat is to be supplied from external burners that use a part of the natural gas as fuel. 70% of the natural gas is reformed while the other 30% is used in the furnace as fuel. Commonly, the reactor consists of rows of tubes 8 inches in diameter, 30 feet long in order to absorb heat.

The flue gas which leaves the primary reformer radiant section at about $1760^{\circ}F$ is recovered by several preheat coils in the convection section. The fule gas leaves through the reformer stack at $390-480^{\circ}F$. The heat recovery coils are:

1. Waste heat boiler, the steam of which is used as the steam in the primary reforming.
2. Heating of natural gas from ambient temperature to $930-1020^{\circ}F$ for primary reforming reaction.
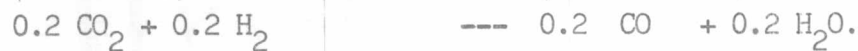3. Heating of air to be used in the secondary reformer.

3.3   Secondary Reforming

About 90% of the CH_4 through the primary reformer is converted to H_2. The partially reformed gas leaves the primary reformer at $1310-1510^{\circ}F$ and enters the secondary reformer where it is mixed with air to produce a synthesis gas having a $H_2:N_2$ ratio of 3:1. Heat required to complete the reforming reaction is obtained by the combustion of the air/gas mixture over a bed of Ni-base catalyst similar to the primary reformer catalyst.

Air is mixed with the gas to form a reaction in the catalyst of the secondary reformer as follows:

Combustion above Catalyst (exothermic)

$$0.07 \; O_2 + 0.3 \; N_2 + 0.15 \; CO \; \text{---} \; 0.15 \; CO_2 + 0.3 \; N_2$$

$$0.2 \; O_2 + 0.8 \; N_2 + 0.4 \; H_2 \; \text{---} \; 0.4 \; H_2O + 0.8 \; N_2$$

Reforming and shift in catalyst (endothermic)

$$0.2 \; CH_4 + 0.2 \; H_2O \; \text{---} \; 0.2 \; CO + 0.6 \; H_2$$

$$0.2 \; CO_2 + 0.2 \; H_2 \; \text{---} \; 0.2 \; CO + 0.2 \; H_2O.$$

The CO formed from this unit is to be converted to CO_2, so the gas is to be sent forward to the CO shift converter.

The nearly completely reformed synthesis gas leaves the secondary reformer at 1740-1830°F and is cooled by a waste heat boiler to about 680°F. The boiler produces steam at approximately 1500 psig which is used to drive turbomachinery.

3.4   CO Shift Conversion

The function of the shift conversion is to burn CO to CO_2, gaining more H_2 and easening the removal of impurity; carbon oxides. Cooled synthesis gas leaving the reformer sections containing about 12% CO and 8% CO_2 as unwanted products. To eliminate the CO, the gas is passed over a bed of chromium oxide/promoted iron oxide catalyst in the high-temperature shift converter which operates at 625-1020°F. CO converts to CO2 and more H_2 is produced with the following exothermic reaction:

$$CO + H_2O \; \text{------} \; CO_2 + H_2$$

The gas leaving the high-temperature shift converter at $780^{\circ}F$ is cooled to about $450^{\circ}F$ in a heat exchanger. It is then passed over a bed of copper oxide-zinc oxide catalyst in the low-temperature shift converter. This step reduces the CO content of the synthesis gas to about 0.4%. The gas is cooled to $200^{\circ}F$ and enters the CO_2 removal system.

As the shift conversion equilibrium favors the low temperature and the rate of reaction increases as to temperature, the conversion is separated into two parts, namely, high-temperature shift conversion and low-temperature shift conversion. The high-temperature shift conversion unit and the low-temperature shift conversion unit are separated apart by a waste heat boiler in order to cool the gas and a desulfurisation tank to safeguard the low-temperature shift converter catalyst because the high-temperature shift converter catalyst can tolerate up to a certain limit of sulfur compound while the low-temperature shift converter catalyst is very sensitive and can be poisoned by sulfur compounds.

The sulfur-compound absorption bed is designed to work for two years, then, the absorption material is to be replaced by active one. The materials for this design is ZnO.

The CO shift conversion should be effective in order to minimize loss of purge gas from the system. The CO_2 formed is rather easier to remove from the system than CO. The shift conversion is rather important for this reason; both the CO or CO_2 remaining in the system can poison the synthesis catalyst, and should be removed or transformed to other undangerous gases and purged. The transformation of carbon oxides to undeangerous gases, methane, is the methanation process.

3.5 CO_2 Removal

Following the shift conversion, CO_2 must be removed from the mixture of H_2 and N_2. About 1.2 metric tons of CO_2 are produced for every metric ton of ammonia manufactured (Strelzoff, 1975).

An effective unit of carbon dioxide removal is very important. For efficient conversion to ammonia, the H_2/N_2 synthesis gas must contain no more than 10 ppm carbon oxides.

The process of purification of synthesis gas in this design is the hot carbonate process. A comparison of MEA process and hot carbonate process is shown in Table III-2. It was developed recently in 1950s which has the following advantages over the MEA method:

1. Less capital investment
2. Less operating costs.

This hot carbonate process is favoured at carbon dioxide partial pressures of 20 psig and higher in the inlet gas. The generation efficiency (ft^3 CO_2 regenerated per lb steam utilized) varies directly with the carbon dioxide partial pressure. Potassium carbonate concentration is 25%; the carbon dioxide pickup at this concentration is 3 ft^3/ga. The removal of hydrogen sulfide is 10 to 15 times faster than that of carbon dioxide at the usual operating temperatures. Corrosion inhibition of the carbonate-bicarbonate solution by either dichromate, vanadium pentoxide, or vanadate at concentrations of 1,000-4,000 ppm is practiced to permit use of carbon steel for most of the equipment.

Table III-2

Process Comparisons: MEA-Benfield

For Gas Feed Rate of 2.5 MM SCFH, 400 psig, 20% CO_2

purified gas content of 1,000 ppm CO_2

Item	MEA solution	Benfield hot potassium carbonate process	Promoted Benfield carbonate process
Relative capital investment	1.00	0.85	0.68
Regeneration heat MM BTU/h	136	68	42-60
Solution flow rates, g/h	167,000	158,000	125,000
Cooling duty MM BTU/h	124	74	58-76

Source: Benson, 1974

3.6 Methanation

All CO_2 absorption systems leave a small amount (less than 1%) of residual carbon oxides in the gas. Both CO_2 and residual carbon monoxide must be removed; otherwise they will poison most synthesis catalysts. Removal is accomplished by a catalytic methanation process. Heat of reaction is recovered from the methanator effluent by exchange with boiler feedwater.

The synthesis gas is reacted over a Ni-containing catalyst (NiO on alumina) at 580°F and pressure at 400 psig. The reactions in the methanator are:

$$CO + 3 H_2 \text{-------} CH_4 + H_2O$$

$$CO_2 + H_2 \text{-------} CO + H_2O$$

$$CO_2 + 4 H_2 \text{-------} CH_4 + 2 H_2O.$$

These reactions are the reverse of that occuring in steam reforming of methane. Reversal is accomplished through the use of lower temperatures and absence of excess water, both of which favour the formation of methane.

The methanator exit gas is cooled to $100^{\circ}F$ and contains less than 200 ppm carbon oxides. Condensate is removed in a process condensate drum. The final synthesis gas at $100^{\circ}F$ and about 400 psig contains H_2 and N_2 in a ratio of 3:1 and is ready to go to the main step of forming ammonia, the ammonia synthesis.

3.7   Ammonia Synthesis

The synthesis gas is compressed in several stages to 3,000 psig. It is also mixed with recycled synthesis gas from the reactors. The combined gas stream is cooled to $-10^{\circ}F$ in a refrigeration cooler. Condensed ammonia is separated from the unconverted gas in a liquid-vapor separator. The gas is preheated to about $360^{\circ}F$ before entering the converter. At this point, the synthesis gas contains hydrogen and nitrogen in the proper 3:1 ratio, along with 14% inerts and about 4% ammonia.

In the converter, synthesis gas is dispersed through a promoted Fe_3O_4 catalyst (an iron oxide catalyst whose activity is increased or promoted by the addition of oxides of aluminum or potassium). The gas exiting the catalyst beds in the converter is about $700^{\circ}F$ and contains approximately 25% ammonia and 14% inerts. This hot gas is used to preheat

boiler feedwater for the steam system and is then heat exchanged with feed gas to the converter.

The ammonia-rich gas is recycled through the synthesis compressor before being cooled to condense the ammonia. A small portion of the overhead gas is purged to prevent accumulation of inerts in the circulating gas system. The purge gas is cooled to $-10^{\circ}F$ to minimize loss of ammonia, and is burned as fuel in the primary reformer.

Liquid ammonia from the primary, secondary and purge separators is collected in the letdown separator, where the ammonia is flashed to atmospheric pressure at $-27^{\circ}F$ to remove additional impurities such as argon. The flash vapors are condensed in a pressure letdown chiller. Anhydrous liquid ammonia of high purity is transferred from the letdown separator to low-temperature atmospheric pressure storage.

3.8   Ammonia Storage

It is a practice to store ammonia at atmospheric pressure. As the ammonia in the storage vessels boils, the vapors are refrigerated and return to the tank. From storage, the ammonia is shipped out by truck, rail, barge, or tanker.

Table III-3 Stock Table

No. of Stream	01	10	11	12	13	14
H_2						7.08
CO						.91
CH_4	3.00	3.00		3.00	3.00	1.01
CO_2						1.09
H_2O			10.52	10.52	10.52	7.44
N_2						
Ar						
NH_3						
O_2						
Total lb-mole/hr $\times 10^3$	3.00	3.00	10.52	13.52	13.52	17.52
T, °F	90	90	750	450	950	1450
P, psi	500	500	600	500	500	500
$\bar{T}_c$, °R	343.9	343.9	1165.3	983	983	585
$\bar{P}$, atm	45.8	45.8	218.3	180	180	107
MW	16	16	18	17.55	17.55	13.56

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Table III-3 (continued)

No. of Stream	141	142	150	151	21	211
H_2			8.19	8.19	9.64	9.64
CO			1.95	1.95	0.50	0.50
CH_4			0.04	0.04	0.04	0.04
CO_2	.00	.00	1.01	1.01	2.47	2.47
H_2O			8.27	8.27	6.81	6.81
N_2	3.21	3.21	3.21	3.21	3.21	3.21
Ar	0.04	0.04	0.04	0.04	0.04	0.04
NH_3						
O_2						
Total lb-mole/hr $\times 10^3$	4.11	4.11	22.71	22.71	22.71	22.71
T, ^{O}F	350	1200	1750	700	780	450
P, psi	500	500	400	400	400	400
$\bar{T}_c$, ^{O}R	238.08	238.08	524.48	524.48	473.32	473.32
$\bar{P}$, atm	37.02	37.02	95.28	95.28	84.57	84.57
MW	28.94	28.94	15.70	15.70	15.70	15.70

Table III-3 (continued)

No. of Stream	22	231	23	24	241	25
H_2	10.01	10.01	10.01	10.01	10.01	9.63
CO	.13	.13	.13	.13	.13	
CH_4	.04	.04	.04	.04	.04	0.17
CO_2	2.84	2.84	2.84			
H_2O	6.44	6.44	.18	.18	.18	.31
N_2	3.21	3.21	3.21	3.21	3.21	3.21
Ar	0.04	0.04	0.04	0.04	0.04	0.04
NH_3						
O_2						
Total lb-mole/hr $x10^3$	22.71	22.71	16.45	13.59	13.59	13.35
T, ^oF	450	200	200	200	500	580
P, psi	400	400	400	400	400	400
$\bar{T}_c$, ^oR	460.3	460.3	191.05	116.53	116.53	129.42
$\bar{P}$, atm	81.84	81.84	29.74	20.70	20.70	22.97
MW	15.70	15.70	14.82	8.74	8.74	8.74

Table III-3 (continued)

No. of Stream	251	26	30	31	32	33
H_2	9.63	9.63	23.61	23.61	23.61	23.61
CO						
CH_4	.17	.17	3.65	3.65	3.65	3.65
CO_2						
H_2O	.31					
N_2	3.21	3.21	7.87	7.87	7.87	7.87
Ar	0.04	0.04	.84	.84	.84	.84
NH_3			7.64	7.64	7.64	2.05
O_2						
Total lb-mole/hr $\times 10^3$	13.35	13.05	43.62	43.62	43.62	38.02
T, $^{\circ}F$	100	100	300	100	- 10	- 10
P, psi	400	400	3000	3000	3000	3000
$\bar{T}_c$, $^{\circ}R$	129.42	104.86	234.50	234.50	234.50	160.14
$\bar{P}$, atm	22.97	18.34	37.02	37.02	37.02	25.86
MW	8.74	8.69	11.22	11.22	11.22	10.37

Table III-3 (continued)

No. of Stream	34	35	36	37		
H_2	23.61	14.67	.68	13.99		
CO						
CH_4	3.65	3.65	.17	3.48		
CO_2						
H_2O						
N_2	7.87	4.89	.23	4.66		
Ar	.84	.84	.04	.80		
NH_3	2.05	8.02	.37	7.64		
O_2						
Total lb-mole/hr $\times 10^3$	38.02	32.07	1.49	30.57		
T, $^{\circ}F$	360	700	300	300		
P, psi	3000	3000	3000	3000		
$\bar{T}_c$, $^{\circ}R$	160.14	391.25	291.25	291.25		
$\bar{P}$, atm	25.76	45.19	45.19	45.19		
MW	10.37	12.30	12.30	12.30		