

THEORETICAL ANALYSIS OF CYCLIC PROCESSES  
FOR PYROLYSIS OF PETROLEUM OILS

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INTRODUCTION

The most severe problem which faces any utility is the ability to supply gas, water, or electricity during periods of peak demand. In the case of the natural gas industry, the gas comes from wells which are generally a great distance from the point of use. This requires the construction of very expensive transmission pipelines. To use these pipelines economically, it is necessary to run them at near their maximum capacity at all times. If this is to be done during periods of low consumption, the pipelines will be incapable of furnishing the required gas during periods of high consumption and means of supplementing gas will have to be found.

In practice, the gas industry meets this problem in a large variety of ways. For example, additional uses of gas during periods of low consumption are encouraged by selling the gas on an interruptible basis at a low cost. This means that when non-interruptible customers - principally residential - require gas the interruptible service can be shutoff. Gas is quite generally sold to industrial manufacturers on this basis. These concerns meet the problem which confronts them when their service is interrupted by putting in standby facilities such as combination burners which can burn oil as well as gas. A second method, very commonly used by the gas industry, is to store the gas near the point of consumption. This method has been used quite extensively where natural storage facilities exist. Such facilities might be depleted oil or gas wells, aquifers, or underground storage caverns which occur naturally and which are capable of containing gas at relatively high pressure. At the present time there is great interest in liquefying natural gas and storing it in various types of containers near the point of consumption.

While all of the above means are used to meet this problem there still remains, in many localities, a problem of meeting the high peaks of demand which occur during extremely cold weather. Commonly, such periods are only a few days in length and occupy only from ten to thirty days of the year. In the creation of facilities to handle such peaks it is apparent that investment cost is a paramount item. If, for example, the average annual usability of the facility is 15 days, the fixed charge on the investment must be carried by 15 days of operation rather than 365 days. Therefore the fixed charge must be multiplied by a factor of nearly 25 in arriving at the cost which must be added to the cost of the gas which is furnished during the peak period.

One of the methods used to meet the peak demands is storage of propane, which can be blended with air when needed and sent out with the natural gas which is arriving via the pipeline. As mentioned above, storage of natural gas either in underground facilities or as liquid natural gas can be used to meet the problem. In some sections of the United States, principally the northeastern sections, it is advantageous to store oil and to gasify the oil when the supplemental gas is required. The present paper is concerned with the oil gasification process.

A large number of processes have been developed to gasify oil. Among these are highly sophisticated processes such as hydrogasification (1,2,3) or thermofor pyrolytic cracking (4,15), which are both continuous processes capable of gasifying a wide range of feedstocks. They are found to be unsuitable, however, because of their high investment cost. The cyclic processes to be discussed here most nearly meet the requirements of the gas utility industry in the important aspect of having low investment cost.

#### GENERAL PROCESS CONSIDERATIONS

When petroleum oils are heated to about 1100°F. or higher, pyrolysis occurs, that is, the larger oil molecules undergo thermal cracking to form a wide variety of end products. The chemistry and the chemical kinetics of this process has been thoroughly studied and reported by Linden *et al* (6,7). During the thermal cracking process coke, tar, aromatic liquids, and butadienes are formed, as well as permanent gases such as methane, ethane, ethylene, hydrogen, etc., which can be used as substitutes for natural gas. The gas issuing from the thermal cracking device is, therefore, cooled to condense the tar and scrubbed with light oil to remove objectionable constituents such as benzene, toluene and the butadienes. After being properly blended with flue gas to adjust the heating value and density to make it substitutable for natural gas, the product gas is sent to the customer.

In spite of the highly involved chemistry, Linden *et al* (6,7) have shown that the gas resulting from the cracking operation can be characterized by a fairly simple expression; the heating value and products formed are a function of

$$t \theta^{0.06}$$

in which  $t$  is the temperature at which the cracking occurs in °F. and  $\theta$  is the time in seconds. While Linden's work was conducted under essentially isothermal conditions one can derive from it the integrated effects of temperature and time at temperature in a non-isothermal heating process. These relationships will be discussed in a future paper. The present paper is concerned with the heat transfer aspects of an oil gas set (the cyclic heating apparatus) and not directly with the chemical kinetics.

The equipment used to carry out the oil gasification process can, in principle, be extremely simple. It may consist of an insulated shell into which refractory shapes are placed in such a fashion as to provide free access of flowing oil vapors to the surface of the refractory shapes and to allow the refractories to be heated up by a flow of hot flue products. For example, one might lay up conventional firebrick to form parallel walls with spaces between the walls for the passage of the gases. Heat is stored in the refractories by passing a combusted oil and air mixture through the passages. When the desired amount of heat has been stored in the refractory, a small amount of steam is passed through the passages to remove most of the flue products. Then oil mixed with steam is passed through the passages. The oil-steam mixture utilizes the stored heat to vaporize the oil, to heat it to cracking temperature, and to furnish the required heat of cracking. When the stored heat has been removed, a small amount of steam is again passed through the set to remove the last of the oil gas and the heating cycle is again initiated.

In principle, the oil gas set performs simply as a regenerative heat exchange device. A significant difference between the operation of the oil gas set and the regenerators in common industrial use arises from a fact which can be seen in Linden's correlation; i.e., the heating value of the gas product is extremely sensitive to temperature. In any regenerative process the temperature of the stream being heated will be hotter at the beginning of the cycle than it will be at the end. Since temperature has such a pronounced effect in the oil gas process it is necessary to use extremely short cycles to minimize this temperature difference.

#### THE HEAT EXCHANGE PROBLEM

The number of permutations and combinations of ways to accomplish the cyclic heat exchange required in an oil gas operation are limitless. One can choose from a large number of heat exchange materials and there are limitless variations in their size and shape. The process can be operated cocurrent flow (the heating stream and the make (oil) stream traveling in the same direction through the set) or countercurrently (the heating stream flowing through the set in one direction and the make stream in the reverse direction). The heat or make streams can be introduced into the set at a variety of points and the heating air can be preheated from the residual heat in the make stream before the air is combined with oil for combustion on the heating cycle. The problem can be further complicated by carbon deposition, which occurs during the cracking portion of the cycle and which is, of necessity, burned off during the heating cycle. Nearly all of these variations, as well as the chemical kinetics, have been built

into a digital computer program which is capable of describing the details of the process with sufficient accuracy that the computed heating value of the product gas is in very good agreement with actual operating results. A detailed description of this computer program is beyond the scope of the present paper. We will, however, show some very simplified expressions for the heat transfer problem which will give a clear indication as to the important variables in the heat transfer process together with some results of the computer program for a typical cocurrent-flow set.

### Simplified Model

The simplest model of a regenerative heat exchanger is one in which the heating gas and the cooling gas flow through the set in the same direction (parallel flow), and having heat exchange material with an infinite heat capacity. The heat exchange material will then adopt a constant temperature intermediate to the heat and make streams. Thus one can write

$$h_1 A (t_1 - t_{1'}) T_1 = h_2 A (t_1 - t_2) T_2 \quad (1)$$

$$h_1 A (t_1 - t_{1'}) T_1 = -w_1 c_1 T_1 \frac{dt_1}{dx} \quad (2)$$

$$-w_1 c_1 T_1 \frac{dt_1}{dx} = w_2 c_2 T_2 \frac{dt_2}{dx} \quad (3)$$

where

$h$  = heat transfer coefficient - Btu/(hr x ft<sup>2</sup> x °F.)

$A$  = heat transfer area per unit length - ft<sup>2</sup>/ft

$t$  = temperature - °F.

$T$  = time of period - hr

$w$  = mass flow rate of gas per unit open area,  
lb/(hr x ft<sup>2</sup>)

$c$  = specific heat of gas - Btu/(lb x °F.)

$x$  = length in direction of flow - ft

Subscripts

1 = heating gas

2 = cooling gas

1 = heat transfer surface

Equation (1) equates the heat transfer rate multiplied by the period time of the two parts of the cycle, assuming no purge periods. Equation (2) equates the same to the heat given up by the heating gas as sensible heat of temperature change

per unit length along the regenerator. Equation (3) equates the heat lost by the heating stream to the heat gained by the cooling stream.

Equation (1) is used to solve for  $t_1$  in terms of  $t_1$  and  $t_2$ . This result is substituted into Equation (2). Equation (2), with the substitution, is differentiated with respect to  $x$  and the resulting term containing  $dt_2/dx$  is eliminated by using its value from Equation (3). Thus, a second order equation in  $t_1$  is obtained as follows:

$$-a_1 \frac{d^2 t_1}{dx^2} = b \left( 1 + \frac{a_1}{a_2} \right) \frac{dt_1}{dx} \quad (4)$$

$$a_1 = w_1 c_1 T_1$$

$$a_2 = w_2 c_2 T_2$$

$$b = \frac{h_1 T_1 h_2 T_2 A}{h_1 T_1 + h_2 T_2}$$

Appropriate boundary conditions of

$$x = 0, \quad t_1 = t_1^0, \quad t_2 = t_2^0$$

$$x = 0, \quad \frac{dt_2}{dx} = -\frac{b}{a_1} (t_1^0 - t_2^0)$$

$$x = \infty, \quad t_1 = t_2$$

can be applied to the integration of Equation (4) and the related expressions for  $t_2$ , and the final result is

$$\frac{t_1^0 - t_1}{t_1^0 - t_2^0} = \frac{a_2}{a_1 + a_2} \left\{ 1 - \exp \left[ -\frac{(a_1 + a_2) b}{a_1 a_2} x \right] \right\} \quad (5)$$

$$\frac{t_2 - t_2^0}{t_1^0 - t_2^0} = \frac{a_1}{a_1 + a_2} \left\{ 1 - \exp \left[ -\frac{(a_1 + a_2) b}{a_1 a_2} x \right] \right\} \quad (6)$$

To a fair degree of approximation, the temperature rise of the make stream ( $100^\circ$  to  $\sim 1300^\circ\text{F.}$ ) and the temperature drop of the heating stream ( $3000^\circ$  to  $\sim 1700^\circ\text{F.}$ ) are of the same order of magnitude. As a consequence, the values of  $a_1$  and  $a_2$  are also of the same order of magnitude. If the periods and the heat transfer coefficients are also equal, Equation (6) reduces to

$$\frac{t_2 - t_2^0}{t_1^0 - t_2^0} = \frac{1}{2} \left\{ 1 - \exp \left[ -\left( \frac{2}{WCT} \right) \left( \frac{hT}{2} \right) ax \right] \right\} \quad (7)$$

which is trivial except to show that the period time will tend to cancel out under these operating conditions. In addition if  $T_2$  is made lower but not  $T_1$  or  $a_1$ , then  $w_2 c_2$  will have to go up or the set capacity will fall and if  $w_2 c_2$  goes up,  $h_2$  will also rise and  $h_2 T_2$  will tend to stay the same. As a result the effect of the period is very small. The computer program bears this conclusion out as can be seen in Figs. 1, 2, and 3 where the make period has been varied from 43 to 86 seconds without appreciable change in the heating value of the oil gas produced. The heating value of the oil gas is very sensitively related to the temperature the oil reaches as described above.

### Refined Heat Transfer Model

The above very simple treatment of the problem gives no information on the effect of the properties of the heat transfer medium. A better approximation to the actual problem can be obtained in the following way.

If a sine wave temperature variation having an amplitude equal to  $(t_1 - t_0)$  is impressed upon a heat transfer material having real properties,  $c_1$ ,  $\rho_1$ ,  $k_1$ ,  $\alpha_1$

where

$$\rho_1 = \text{density} - \text{lb/ft}^3$$

$$k_1 = \text{conductivity} - \text{Btu/hr} \times \text{ft} \times \text{°F.}$$

$$\alpha_1 = \text{diffusivity} - \text{ft}^2/\text{hr}$$

and if  $h_1$  is equal to  $h_2$ , it can be shown (8) that the surface temperature of the heat transfer medium will oscillate between  $t_{1,1}$  and  $t_{1,2}$  in such a way that

$$t_{1,1} - t_{1,2} = F (t_1 - t_2) \quad (8)$$

where  $F$  is a constant and is given by

$$F = \left[ 1 + \frac{2k_1}{h} \sqrt{\frac{\pi}{2\alpha_1 T}} + \frac{\pi k_1^2}{\alpha_1 T h^2} \right]^{-1/2} \quad (9)$$

Equations (1) and (2) may be revised to account for the fact that the heat exchange medium has an average surface temperature which is higher than  $t_1$  during the heating cycle and cooler during the cooling cycle.

$$h_1 A (t_1 - t_{1,1}) T_1 = h_2 A (t_{1,2} - t_2) T_2 \quad (1a)$$

$$h_1 A (t_1 - t_{1,1}) T_1 = -w_1 c_1 T_1 \frac{dt_1}{dx} \quad (2a)$$

If Equation (8) is used in combination with (1a) and (2a) and the same procedure followed as shown above the resulting solutions will be exactly as in Equations (5) and (6) except for the definition of  $b$  which becomes  $b'$ .

Some values of  $F$  have been computed for reasonable values of the various parameters and using a fireclay and a silicon carbide refractory as the heat exchange medium. Table I shows the properties of these two refractories

Table I

<u>Material</u>	<u>k</u>	<u>c</u>	<u><math>\rho</math></u>	<u><math>\alpha</math></u>
Fireclay	0.88	0.295	130	0.023
Silicon Carbide	9	0.289	160	0.195

Silicon carbide represents a nearly optimum material while fireclay represents about the least expensive material which has sufficient structural strength under the conditions of use. Table II shows the assumed values of  $T$  and  $h$  and the resulting values of  $(1-F)$ .

Table II

<u>Period Time,</u> <u>T, min.</u>	<u>Heat Exchange</u> <u>Medium</u>	<u>1-F</u>	
		<u>h = 5</u>	<u>h = 10</u>
1.5	Fireclay	0.93	0.87
1.5	Silicon Carbide	0.98	0.96
2.5	Fireclay	0.90	0.84
2.5	Silicon Carbide	0.97	0.94

This table shows that the thermal properties of the heat exchange material are not an overriding consideration. The largest effect is at an  $h$  of 10 and a period of 2.5 minutes (5 minute cycle), where the silicon carbide shows a 12% higher value of  $(1-F)$ . This would allow the use of 12% less surface area of silicon carbide (less refractory) or 12% more production of oil gas with the same surface and no change in  $h$  (same amount of refractory but rebricked to keep the gas velocities unchanged).

In an extensive monograph on regenerative heat transfer, Hausen (8) derives equations which are very similar to those given above but which cover long cycles as well as short ones. If the two are compared for the conditions of interest in oil gas sets the quantitative results are very close although the algebraic form of expressions showing the effect of the properties of the heat exchange medium are quite different. In place of  $F$  given above in Equation (9), Hausen has

$$1 - \frac{1}{1 + \frac{0.375 h \delta}{k(0.3 + \frac{\delta^2}{\alpha T})^{1/2}}}$$

where

$\delta$  is the brick half thickness - ft

He also has the same harmonic form of combining the values of  $h_1 T_1$  and  $h_2 T_2$ ,  $T_1$  and  $T_2$  as well as  $a_1$  and  $a_2$ .

#### The Computer Model

While the foregoing relationships are very useful to examine the effects of the variables they can not be used to predict actual operating results. Partly this is due to the fact that the results of the cracking reaction are dependent upon time as well as on temperature and in a very complex fashion. The capability of being able to consider the large number of possible ways to construct and operate a set is important.

In addition the heat transfer coefficient during the heating period varies by a substantial amount due to the intense gas radiation in the first several courses of brick and the effective heat capacity of the make stream varies considerably due to heat of vaporization in the first few courses and heat of cracking in the central sections.

Fig. 4 shows an example of a very common cocurrent set design. It is built with two vertical sections with an empty crossover section. This construction comes about because these sets are actually converted carburetted water gas sets. As mentioned earlier there are a large variety of shapes and sizes of this design and many other designs as well.

The open space at the top of the left hand section is required as a combustion section on the heating period. The refractory in the first few courses just below the combustion chamber is usually made of silicon carbide in order to withstand the extreme temperature fluctuations which occur in the switch from hot flue gas (3000°F.) to cold oil and steam (200°F.). The high thermal conductivity and diffusivity of this material greatly minimizes its temperature fluctuation as can be seen in Table II and Equation (9). Below the silicon carbide are courses of bricks which are usually fireclay and which are not always laid up in the same pattern as the silicon carbide.

The crossover section is usually left relatively open but it still provides heat transfer surface which must be included in the computer analysis. The right hand section, which is not necessarily of the same cross section of the left hand section, is partially filled with checkers; usually fireclay. Above this checkerwork there is an open space in which relatively little heat transfer is accomplished but which provides residence time for cracking to continue under nearly isothermal conditions. The exit oil gas is quenched and cleaned up as described earlier.

The computer program is designed so that each of the sections just described can be analyzed with the input data pertinent to it. Generally cracking each section can be subdivided into small layers in order to improve the accuracy of the calculations. In each subdivision the surface area, the heat transfer coefficient and the thermal properties of the gases are computed for the particular conditions which exist at that position. The variation in time of both the refractory and the gases is computed at the subdivision with the refractory temperature being computed as a function of depth into it normal to the gas flow direction. In sections where thermal cracking occurs the heating value and yield of the oil gas are computed as a function of time over the period and time weighted average values calculated.

The cocurrent sets are relatively simple to compute compared to the countercurrent. This is because the temperature of each gas stream is known at their common inlet point to the set. This makes it possible to start at the front, solve the first subdivision and then proceed to the second, etc. It is not inferred that the solution itself is simple but only that the procedure is straightforward. In the countercurrent set this can not be done because the initial gas stream temperatures are known at opposite ends of the set. This makes it necessary to make an "educated guess" for the entire set, run through the solution, "guess again" and repeat until an acceptably close agreement is obtained. This iteration process is superimposed on the iterative processes used at each subdivision and the required computer time is considerably greater.

Typical computer results are shown in Figs. 5, 6, and 7. Fig. 5 shows the heating gas and oil gas temperatures at the beginning and end of each period. Fig. 6 shows the variation in heating value of the oil gas during the make period at various positions in the set. Fig. 7 shows the heating value and yield at the start and end of a period as well as the average values as a function of the length of the set. These results are for an idealized set and do not represent actual operation but actual results would not appear too different in principle.

### CONCLUSION

A highly sophisticated computer program has been developed which is capable of handling both the complex heat exchange relationships and the chemical kinetics involved in cyclic oil gas sets. The program is being used to analyze existing sets and to enable recommendations for improving them to be made. It will also be used to design an optimum oil gas set in the near future.

Closed form solutions of the heat transfer problem have been obtained. These solutions can be used to show the general effects of the parameters and their interrelationships and to approximate the design of the optimum set.

### ACKNOWLEDGMENT

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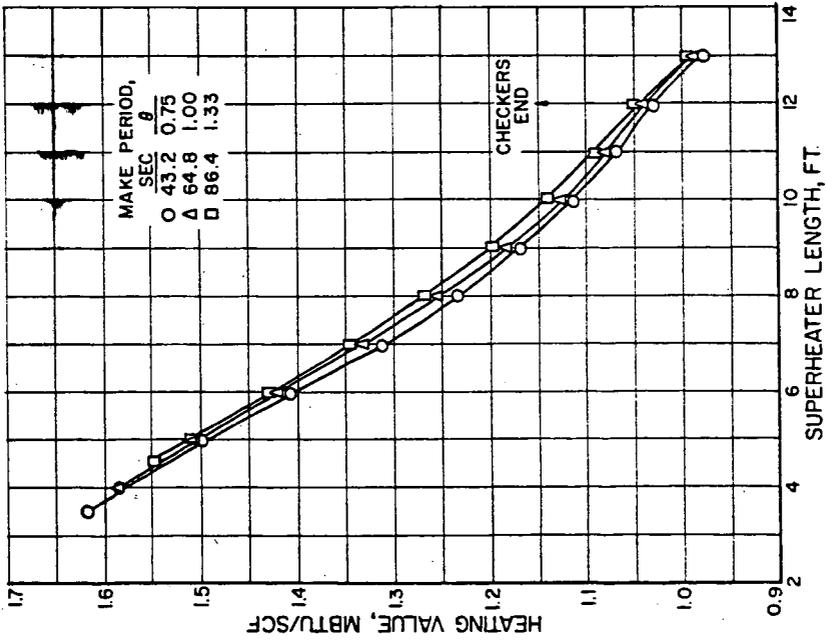


Fig. 1.-EFFECT OF SUPERHEATER LENGTH AND MAKE PERIOD DURATION ON MAKE GAS HEATING VALUE FOR A MAKE OIL RATE OF 852 POUNDS PER SQ. FOOT-HOUR

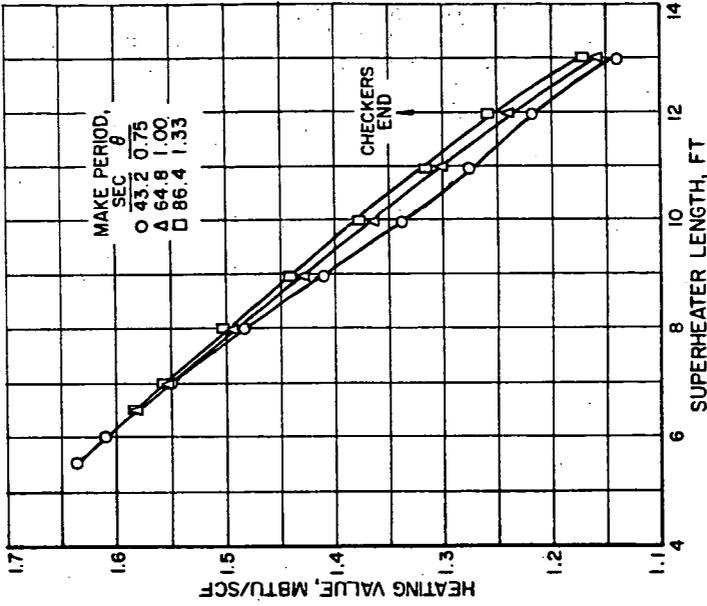


Fig. 2.-EFFECT OF SUPERHEATER LENGTH AND MAKE PERIOD DURATION ON MAKE GAS HEATING VALUE FOR A MAKE OIL RATE OF 1420 POUNDS PER SQ. FOOT-HOUR

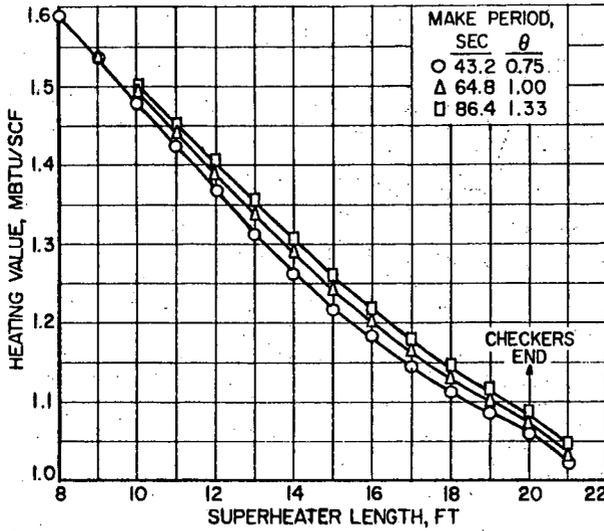


Fig. 3. - EFFECT OF SUPERHEATER LENGTH AND MAKE PERIOD DURATION ON MAKE GAS HEATING VALUE FOR A MAKE OIL RATE OF 1988 POUNDS PER SQ. FOOT-HOUR

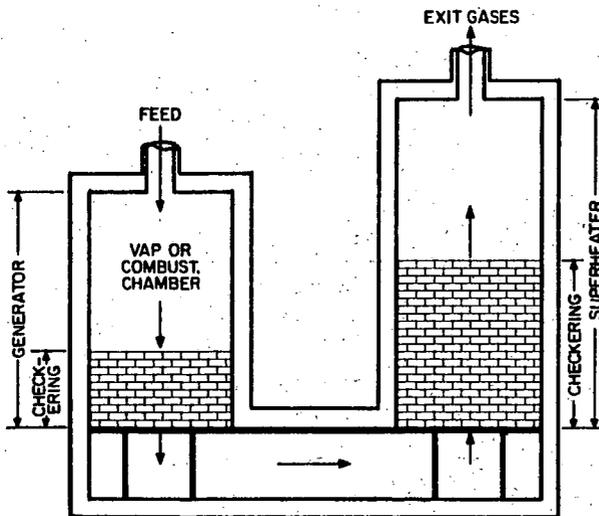


Fig. 4. - SCHEMATIC DIAGRAM OF TWO-SHELL COCURRENT OIL GAS SET

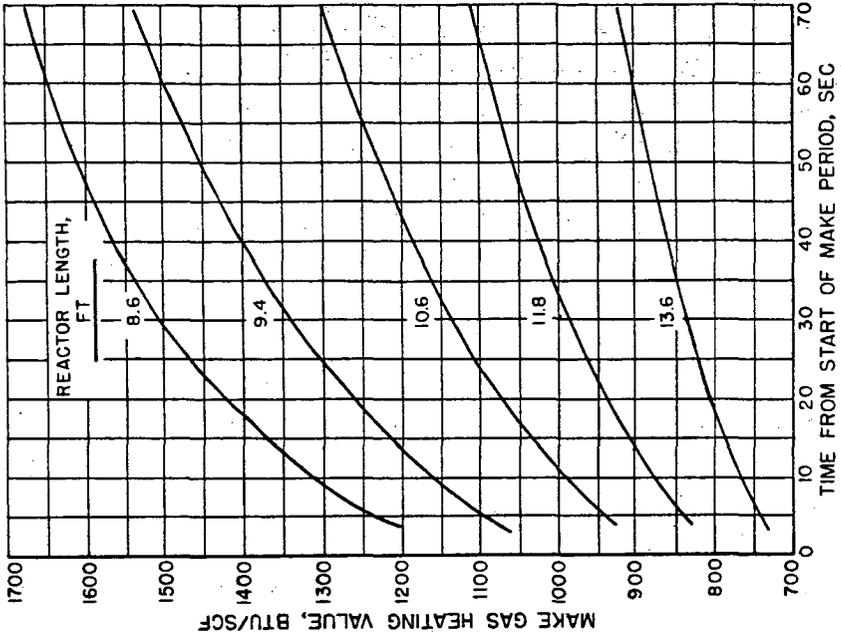


Fig. 6.-EFFECT OF MAKE TIME AND REACTOR LENGTH ON MAKE GAS HEATING VALUE

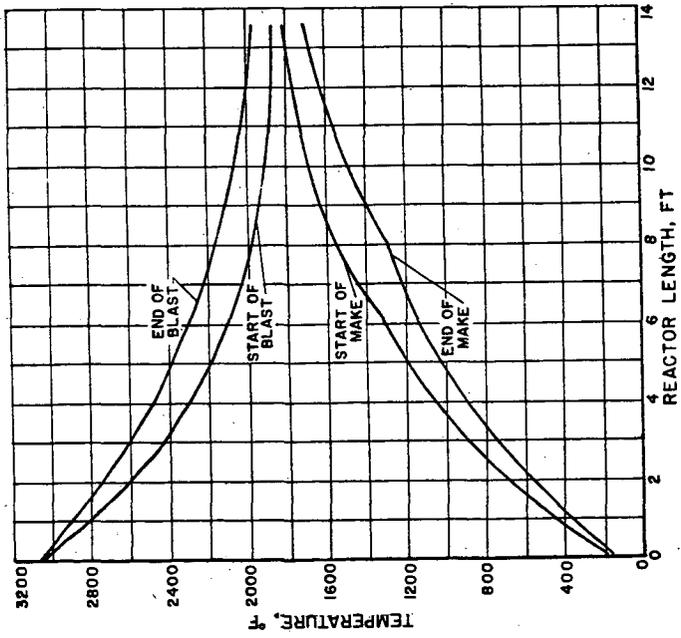


Fig. 5.-GAS TEMPERATURE PROFILES IN CONCURRENT REACTOR

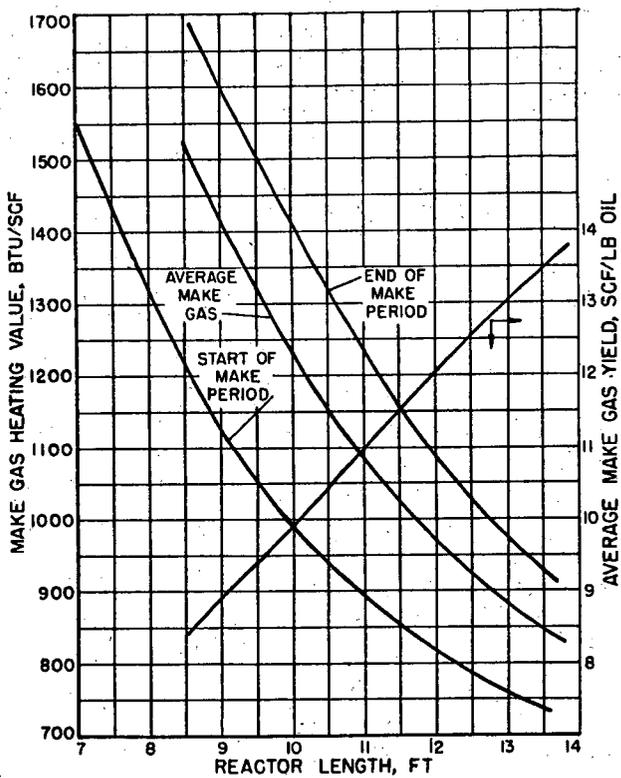


Fig. 7.-EFFECT OF REACTOR LENGTH ON MAKE GAS HEATING VALUE AND AVERAGE MAKE GAS YIELD