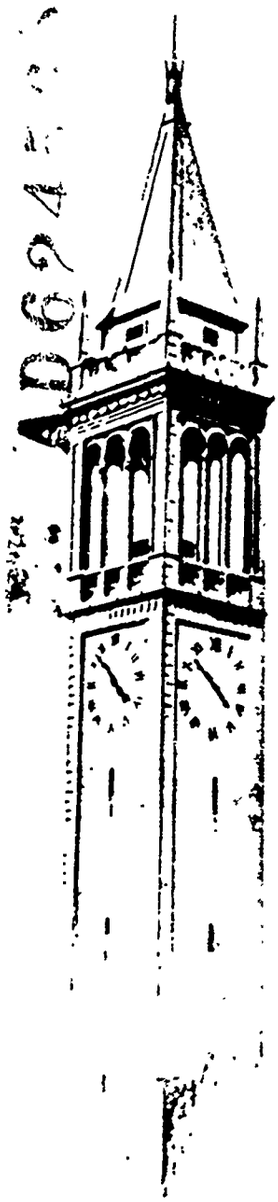

CALCULATION OF ENGINE PERFORMANCE USING AMMONIA FUEL

II. DIESEL CYCLE

by

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Technical Report No. 3

Under Contract
DA-04-200-AMC-791(X) Ammonia Fuel
Army Material Command
R & D Directorate
Chemistry and Materials Branch

Project Director
E. S. Starkman

Summary

A digital computer program has been used to predict theoretical performance for ammonia as a fuel for Diesel engines. The theoretical model employed is the Diesel cycle, and products of combustion have been treated as a chemical equilibrium system. Results are presented for ammonia and in addition for cetene, a common hydrocarbon fuel. It is thus possible to directly compare the performance predicted for ammonia to that predicted for commonly employed hydrocarbon fuels.

The following conclusions regarding performance of ammonia are based upon this work:

1) In the event of developments leading to successful combustion of ammonia in Diesel engine application, ammonia would be expected to yield up to 10% more power output than typical hydrocarbon fuels operating under the same conditions.
2) The thermal efficiency obtained with ammonia would be expected to be greater than that for hydrocarbon fuels by as much as 20%.
3) Specific fuel consumption for ammonia may be expected to be approximately 2-1/2 times greater for ammonia than for hydrocarbon fuels.
4) The exhaust concentration of nitric oxide resulting from the use of ammonia should be substantially less than that produced by hydrocarbon fuels.

CALCULATION OF ENGINE PERFORMANCE USING AMMONIA FUEL

II. Diesel Cycle

INTRODUCTION

This is the third in a series of reports concerning the performance of ammonia as an internal combustion engine fuel. The first[1] presented the general thermodynamic properties of combustion products of ammonia-air mixtures at chemical equilibrium. These properties were calculated for a wide range of temperatures, pressures and air-fuel mixture ratios. The second report[2] was concerned with the results of a theoretical study of ammonia performance as a spark ignition engine fuel using the Otto cycle as a model. The present report involves the prediction of compression ignition engine performance with ammonia. In this case the Diesel cycle is used as a theoretical model. The final report of this series will deal with Brayton cycle performance and pertains to the operation of gas turbine engines.

As pointed out in the previous reports of this series, an important problem arising in the theoretical analysis of internal combustion engine performance is determination of the thermodynamic properties of the working fluid. If these properties are known or may be determined at each point of the cycle of operation of a given engine, then the resulting engine performance may easily be computed using fundamental thermodynamic relationships. As an example of a simple system with known properties, we could consider a hypothetical engine with working fluid consisting of a single pure substance and with combustion replaced by a simple prescribed heat transfer process. In this case properties for any point in the cycle could easily

be computed, and the complete cycle analysis performed.

Unfortunately, however, in the operation of a real engine, a number of factors lead to significant deviations from the performance predicted by such a simple analysis. These factors include the chemically reactive nature of the working fluid, the finite time required for initiation and completion of real combustion processes and the occurrence of heat losses from the working fluid to surrounds.

At the temperatures encountered in representative combustion processes, many normally stable chemical pecies such as H_2O, CO_2, and even the diatomic species H_2,O_2, and N_2 tend to dissociate forming such compounds as OH, CO, NO and the atomic species O, H, and N. The working fluid thus takes on a chemically reactive nature and specification of its chemical composition and resulting thermodynamic properties becomes quite complex. The working fluid then varies continuously in composition throughout the combustion and expansion processes.

If it may be assumed that the sequence of events occurring in the engine cycle is sufficiently slow that time is available for continuous equilibration of chemical reactions, then the well established principle of chemical equilibrium may be used to compute the chemical equilibrium working fluid composition at any point of the cycle. According to thermodynamic principles the composition of any equilibrium, single phase chemically reactive system is completely determined by specification of any two thermodynamic variables, for example, pressure, temperature, volume, entropy or

energy. In this case when two properties are known for any given state point of the engine cycle as example, pressure and enthalpy, then, in principle, the chemical composition and hence the remaining properties for the equilibrium reactive mixture may be computed. The detailed methods of application of equilibrium techniques to the Diesel cycle analysis will be given in a later section of this report.

It is well known that for real systems, significant time delays are inherent in initiation and completion of combustion processes. This fact leads to further deviation of real cycle processes from those of the more simple theoretical models. Analysis of the combustion process in the Diesel engine involves complexities at several physical levels. First arises the problem of diffusion of fuel vapor from the liquid fuel droplet into the surrounding air, generally in turbulent motion. Second, on a microscopic level consideration must be given to the mechanisms of chemical reaction involved in propagation of the flame. At present, these processes are little understood and the possibility of theoretical prediction of burning rates must be discarded. For this reason, it is usually assumed for purposes of analysis that fuel injection may be controlled such that combustion occurs as a constant pressure process beginning at the top center piston position and terminating with complete combustion of the prescribed quantity of fuel.

An additional influence upon deviation of real engine performance from that predicted by simple theoretical models is the loss of heat from the high temperature combustion products to the surrounding engine structure.

It is known that in general approximately 20% of the energy supplied to the engine will be lost by way of heat transfer to the surrounds. The influence of such heat losses upon engine performance depends not only on the total quantity of heat dissipated but also upon the distribution of dissipation over the cycle events. The heat transfer calculation required in predicting the heat loss rate throughout the cycle would at best be quite complex and of questionable validity. For this reason it is often assumed in theoretical cycle analyses that heat transfer effects may be neglected.

It is readily evident that a theoretical cycle analysis which neglects the effects of finite combustion time and heat transfer losses will yield engine performance predictions exceeding the performance to be realized from a real engine. Detailed consideration of the processes of both real and theoretical engine cycles leads however to the conclusion that the influence of finite combustion times and of heat losses upon comparitive results will be of minor concern.

For example in the determination of the influence of a particular parameter, theoretical analyses neglecting heat transfer and burning velocities may be carried out. The results obtained will deviate from those to be expected from a real engine on an absolute basis. However if it may be assumed that heat transfer rates and burning velocities remain essentially unchanged with variation of the given parameter, then comparative or relative results obtained for different values of this parameter will be the same as relative results expected from the real engine. It is therefore

evident that if real engine performance is known for a given value of the parameter of interest, then theoretically predicted values may be scaled to real engine performance to yield a complete performance curve for the real engine.

This type of analysis has been extended to consideration of the influence of fuel composition upon engine performance. It was desired to predict the performance of a yet untested fuel, ammonia. A complete theoretical cycle analysis has been carried out for the fuel under study and an identical analysis has been carried out for a fuel (cetene) whose real performance is well-known from experimental measurements. It was then possible to scale the predicted results for the fuel under study to those to be expected from real engine operation.

Specifically, the object of this work has been to predict the performance of ammonia as a compression ignition engine fuel. The theoretical model employed is the traditional Diesel cycle with analysis of combustion and expansion processes incorporating properties of chemical equilibrium combustion products corresponding to the fuel air mixture considered. The effects of heat transfer and burning velocity have been neglected, and as a consequence the validity of this comparative analysis requires that burning velocities and heat transfer rates be substantially the same for ammonia and the reference fuel, cetene (Hexadecene).

It is known that in general, burning velocities associated with ammonia - air mixtures are much lower than those for hydrocarbon - air mixtures. It is

thus apparent that the above restriction concerning the invariance of burning velocity with fuel type may not be valid. Indeed the primary problem in practical development of ammonia as an engine fuel is the augmentation of ammonia-air burning velocity with the velocities of hydro-carbon air mixtures as desired upper limits. In this sense the analysis presented here may be viewed as predicting an upper limit of comparative engine performance for ammonia. This upper limit might serve, for example, to indicate, in the development of an engine, the degree to which the full potential of the fuel has been realized, or as an indication of whether at a given point of development further work on augmentation of fuel burning velocity would be feasible or justifiable.

Computations involved in the theoretical analysis have been carried out on an I.B.M. 7094 digital computer. The thermodynamic properties of combustion products employed in this work are those presented in Technical Report One of this series[1]. The source of fundamental thermochemical data for this and previous work was the Joint Army, Navy, Air Force Thermo Chemical Tables[3].

METHOD OF CALCULATION

The Diesel cycle, used as a theoretical model for this analysis is presented in its simplest form in Figure one. In terms of elementary thermodynamic processes, the cycle consists of induction of fresh charge of air, 5-1, compression of combustion air, 1-2, constant pressure combustion, 2-3, isentropic expansion of combustion products with production of work, 3-4,

and "blow-down" of expanded combustion products to atmospheric pressure, 4-1. This cycle has been programmed for analysis using an IBM type 7094 digital computer. The specific analytical techniques employed are best described in terms of the elementary cycle processes.

I) Induction

Referring agin to Figure 1, the induction process occurring between state points 5 and 1 consists of mixing of fresh air at ambient temperature T_A with the residual fraction, f, of burned products of combustion at temperature T_f. The values of f and T_f are not known a-priori and must be assumed at the outset. The iterative procedure employed in testing and adjusting these values will be discussed in a later part of this report.

Since the induction process occurs at constant pressure, the total enthalpy of the system must remain constant. Thus, for a system based on a total working fluid mass equivalent to that of 1 lb. air plus the prescribed quantity of fuel,

$$M_A\ (1-f)\ h_A + f\ H_f = M_A\ (1-f)\ h_{A_-} + fH_{f1} \tag{1}$$

or assuming $(C_p)_f \simeq (C_p)_A$

$$M_A\ (1-f)(C_p)_A(T_A - T_{A0}) + f\ H_f = M_A(C_p)_A(T_1 - T_0) \tag{2}$$

Then,

$$T_1 = T_0 + \frac{M_A\ (1-f)(C_p)_A(T_A - T_0) + f\ H_f}{M_A\ (C_p)_A} \tag{3}$$

where: M_A = moles air per lb. air

f = residual fraction of combustion products

T_1 = calculated temperature of state point 1

T_A = ambient air supply temperature

T_0 = datum state temp. (298° k or 537° R)

H_f = enthalpy of residual fraction of combustion products based on combustion of air plus fuel

$(C_p)_A$ = specific heat of air - Btu/lb-mole-$^\circ$R

$(C_p)_f$ = specific heat of residual products Btu/lb-mole-$^\circ$R

The assumption that the specific heat of residual products is the same as that of air leads to an error of less than one percent since the residual fraction usually comprises less than 1% of the mixture and also since the main contribution to the specific heat of the residual is that of N_2 which is also the case for air.

II) Compression

With determination of the initial temperature, T_1, it is assumed that the fresh charge is compressed isentropically to state point 2. The process is divided into 10 equal volume increments, k = 1, 2 ---- 10 during which compression occurs isentropically.

The variation of specific heats during compression is small relative to the variation of the primary variables, as example, energy, temperature, and pressure. It is therefore assumed that the specific heats ratio, γ,

remains constant during each of the compression increments. Compression is then carried out as follows:

$$E_{k+1} = E_k + \frac{P_k V_k^{\gamma_k}}{\gamma_k - 1} \left[V_{k+1}^{\gamma_k - 1} - V_k^{\gamma_k - 1} \right] \tag{4}$$

$$T_{k+1} = T_k \left(\frac{V_k}{V_{k+1}} \right)^{\gamma_k - 1} \tag{5}$$

$$P_{k+1} = P_k \left(\frac{V_k}{V_{k+1}} \right)^{\gamma_k} \tag{6}$$

Where the subscript k represents the k_{th} increment of compression.

Subsequent to the completion of each increment, the value of γ_k is adjusted according to the relation,

$$\gamma_k = \frac{(C_p)_k}{(Cv)_k} = \left[\frac{C_p\ (T_k)}{C_v\ (T_k)} \right] \tag{7}$$

where the specific heats are known functions of temperature. With completion of the 10th increment the properties corresponding to state point 2 have been computed.

III) Combustion

It is assumed that following compression, liquid fuel is injected such that combustion occurs completely at constant pressure, and that the combustion products immediately attain their equilibrium composition. For an adiabatic, constant pressure combustion process total enthalpy must

remain constant, thus:

$$M_3 \left(\sum_{j=1}^{n} X_j \left[H_{js} + H_{j0}\right] \right)_3 = M_2 \left(\sum_{j=1}^{n} X_j \left[H_{js} + H_{j0}\right] \right)_2 - M_f \, \Delta H_v \qquad (8)$$

where: M_3 = total moles product

M_2 = total moles reactant

X_j = mole fraction of species j

H_{j0} = energy of formation of species j at T_0

$H_{js} = H_{jT} - H_{jT_0}$ =sensible enthalpy of species j

M_f = moles fuel

ΔH_v = latent heat of vaporization of fuel

The two variables P_3 and H_3 are thus readily available, and, as previously stated, specification of any two variables completely determines in principle, the composition and properties of the system of equilibrium combustion products. Unfortunately, from a computational viewpoint, the terms $(X_j)_3$ of expression (8), (the product mole fractions), are themselves dependent upon the properties to be so obtained. As a consequence the solution of this system of equations usually involves a trial and error technique in which assumed values for temperature are used in computing composition. An energy balance tested against the known value H_3 then indicates the error in the assumed temperature. This process is in general quite time consuming and often is prone to difficulties with convergence.

The method of calculation employed in the present work provides an alternative to the usual trial and error type of solution. It will be recalled that Technical Report No. 1 (1) presented the equilibrium properties of ammonia - air combustion products over a wide range of temperatures and pressures. This data has subsequently been employed as input to a curvilinear regression program through which the following functional relationships among the appropriate thermodynamic parameters have been generated.

$$V = V\ (H,P) \tag{9}$$

$$S = S\ (E,V) \tag{10}$$

$$P = P\ (E,S) \tag{11}$$

$$T = T\ (E,S) \tag{12}$$

$$E = E\ (S,V) \tag{13}$$

These relations take the form of series expansions in powers of the independent variables. Expression (9) for example, takes the form

$$V = A + B\left(\frac{H}{P}\right) + C\left(\frac{H}{P}\right)^2 + D\left(\frac{H}{P}\right)^3 + E\left(\frac{H}{P}\right)^4 + E\left(\frac{H}{P}\right)^5 + F\left(\frac{H}{P}\right)^6 \tag{14}$$

where the terms A, B, ----, F are constants generated by the regression analysis.

A complete series of such expressions is developed for each fuel-air mixture to be studied, and the resulting terms are applicable quite generally to any problem involving the chemical equilibrium combustion products of that

fuel-air system. For this reason the regression coefficients for ammonia-air combustion products have been tabulated and appear in Tables 1-6.

Knowledge of the two quantities H_3 and P_3 together with the expressions (9) - (13) then leads at once to complete determination of working fluid properties at state point 3 representing completion of the combustion process.

IV) Expansion

With the completion of the combustion process, the high temperature, high pressure products of combustion continue to expand from state point 3 to state point 4. During this expansion further useful work is produced.

For purposes of analysis, it is assumed that expansion proceeds reversibly and adiabatically and further that chemical equilibrium of combustion products is maintained at all times. In this case then the entropy of combustion products will remain constant at that value determined previously for state point three, and at any point of the expansion given by specified cylinder volume V, working fluid composition and properties may be obtained by simultaneous solution of the following system of equations.

$$S = M \sum_j X_j S_j(T) - R \sum_j X_j \ln X_j - R \ln P = S_3, \text{ KNOWN QUANTITY} \quad (15)$$

$$V = \Phi (T, P, X_j), \; j = 1, 2, \ldots, n, \text{ SPECIFIED VOLUME} \quad (16)$$

$$X_j = \Phi_j (T, P), \; j = 1 \ldots\ldots n \quad (17)$$

Again, the usual procedure followed in solution of this system of equations would involve trial and error techniques. However, the previously described regression equations may be used to advantage in simplifying the solution. Specifically, in solving for working fluid properties at point 4, the end of expansion, the following sequence may be employed.

$$S_4 = S_3 = \text{known} \tag{18}$$

$$V_4 = V_2 \times \text{C.R.} \tag{19}$$

$$E_4 = E_4\ (S_4, V_4) \quad \text{(regression)} \tag{20}$$

$$P_4 = P_4\ (E_4, S_4) \quad \text{(regression)} \tag{21}$$

$$T_4 = T_4\ (E_4, S_4) \quad \text{(regression)} \tag{22}$$

Thus each of the pertinent thermodynamic properties corresponding to the end point of expansion is easily obtained by straight forward substitution into the regression equations.

V) Blow Down

At completion of the expansion process as represented by state point 4 of Figure 1, the combustion products remain at a pressure greater than atmospheric. The blowdown process is characterized by opening of the exhaust valve with further expansion of the combustion products to atmospheric pressure. It is again assumed that expansion of those gases remaining in the cylinder occurs reversibly and adiabatically and that combustion products continue to exist in a state of chemical equilibrium. The expelled cylinder

gases expand to a hypothetical volume V_4' dictated by the condition $S_4' = S_4$ and P_4 = 14.7 psia. The pertinent properties of state point 4' are given by the following regression equations,

$$T_4' = T(S_4', 14.7 \text{ psia}) \tag{23}$$

$$V_4' = V(T_4', 14.7 \text{ psia}) \tag{24}$$

$$H_4' = H(S_4', 14.7 \text{ psia}) \tag{25}$$

Following return of the piston to the top center position, a fraction of the combustion products at condition 4' will remain to dilute the incoming charge for the following cycle. This fraction is given by the expression

$$f = V_1/V_4' \tag{26}$$

In the discussion of the induction process it was noted that it was necessary at the outset to assume values for f and for T_4'. The assumed values may now be compared with those computed above and accordingly adjusted. The entire cycle calculation is then repeated until assumed initial values are found to agree satisfactorily with those computed. For this work satisfactory agreement was taken to be a deviation of one percent or less between assumed and computed values of f and T_4'.

CYCLE PERFORMANCE PARAMETERS

With complete determination of working fluid properties at each of the state points indicated in Figure 1, the theoretical prediction of engine performance may be carried out.

I) Work Output Per Cycle

The work obtained from the cycle consists of the expansion work occurring during the constant pressure combustion process in addition to that produced by isentropic expansion less the work required in compressing the fresh air charge plus dilution fraction. According to the first law of thermodynamics, the net work produced per cycle is given by the relation:

$$W = P_2 (V_3 - V_2) + (E_3 - E_4) - (E_2 - E_1) \tag{27}$$

II) Mean Effective Pressure

The mean effective pressure is that pressure measured above the mean compression pressure which, if acting during the entire expansion, would produce a quantity of work equivalent to that actually predicted. For a cycle for which the mean effective pressure was in fact active during the entire expansion, the work produced would be,

$$W = P_{exp} (V_1 - V_2) - P_{com} (V_1 - V_2) \tag{28}$$

hence

$$W = MEP (V_1 - V_2) \tag{29}$$

or

$$MEP = \frac{W}{(V_1 - V_2)} \tag{30}$$

where W is the cycle work given by Equation (27).

III) Thermal Efficiency

The thermal efficiency is defined as the ratio of useful work output obtained from a cycle to the total quantity of heat added to the system during the cycle, that is,

$$\eta_{th} = \frac{W}{Q_{in}} \tag{31}$$

where Q_{in} is the heat added per cycle. In the present case the heat addition is given by the expression,

$$Q_{in} = (LHV) \times W_f \tag{32}$$

where: (LHV) = Lower heat of combustion of the fuel, W_f = weight of fuel supplied per cycle.

Hence

$$\eta_{th} = \frac{W}{(LHV) \times W_f} \tag{33}$$

IV) Specific Fuel Consumption

The specific fuel consumption, an additional measure of engine efficiency, is defined as the weight of fuel consumed per horse-power-hour of engine output. Hence

$$ISFC = \left(\frac{W_f}{W}\right) \times 2545 - \frac{LBS}{HP\text{-}HR}$$

where

W_f = lbs. fuel per cycle

W = work output per cycle - Btu

RESULTS

I) Peak Cycle Temperatures

In the analysis of Diesel cycle engines one of the more interesting calculated parameters is the peak cycle temperature. The peak cycle temperature influences the thermal stresses to which the engine mechanism is subjected, to some extent the quality of combustion, and to a large extent the composition of engine exhaust gases.

Among the factors determining peak cycle temperature for a given engine are the energy content of fuel supplied, the latent heat of vaporization of fuel and the total heat capacity of combustion products for the given fuel, including dissociation effects. In general, a fuel with low energy content, high heat of vaporization and with combustion products having high total heat capacity would be expected to exhibit low peak cycle temperatures.

In comparing ammonia with typical hydrocarbon fuels one observes for ammonia a slightly higher energy content. On the other hand the latent heat of vaporization of ammonia is considerably greater than that of hydrocarbon fuels, and further, the number of moles of products produced in the combustion of ammonia at a given equivalence ratio is considerably greater than the number produced by hydrocarbon fuels at the same equivalence ratio leading

to the conclusion that total heat capacities should be greater for ammonia combustion products than hydrocarbon combustion products.

It would then be expected that the use of ammonia would lead to lower peak cycle temperatures than would the use of hydrocarbon fuels. Figures 2 and 3 indicate that this is so. As shown by Figure 2, predicted ammonia temperatures range from 400 to 800° R less than those predicted for hydrocarbon fuels, depending upon the fuel-air ratio. The temperature difference diminishes as fuel to air ratio decreases, with temperatures converging to the compression temperature in the limit as fuel-air ratio approaches zero.

Figure 3 illustrates the variation of peak cycle temperature with compression ratio for a fuel-air equivalence ratio of 0.6. As indicated, the difference between hydrocarbon and ammonia temperatures is about 400° R and remains nearly constant throughout the range of compression ratios of interest.

II) Engine Power Output

The power output to be obtained from an engine of given volumetric capacity is best given by the indicated mean effective pressure. Figures 5-7 which show predicted cycle mean effective pressures for a number of operating conditions indicate that ammonia would be expected to deliver slightly greater output than typical hydrocarbon fuels.

As noted previously, ammonia exhibits an unusually high latent heat of vaporization. As a consequence, the energy involved in evaporation of the injected liquid charge is significant and tends to reduce the overall

power output predicted. This effect becomes especially pronounced in the regions of lower compression ratio where the heat of vaporization is large relative to expansion work. As compression ratio increases, the work of expansion increases while the heat of vaporization remains essentially constant, and hence the influence of fuel evaporation becomes less significant. This fact is indicated by Figures 5 and 6 which show mean effective pressure as influenced by compression ratio. As compression ratio increases, the mean effective pressure indicated for ammonia increases at a rate higher than that predicted for Cetene, a result of the decreasing significance of ammonia evaporation.

In the discussion of peak cycle temperatures it was noted that for a given fuel-air equivalence ratio, the number of moles product produced in combustion of ammonia exceeds that number resulting from combustion of hydrocarbon fuels. It may be shown that for an engine represented by the Diesel cycle, work output is dependent upon fuel energy content and upon the number of moles product produced in the combustion process. Figure 7 which gives mean effective pressure as influenced by fuel-air ratio indicates that for equivalence ratios ranging from 0.8 to 1.0, predicted ammonia mean effective pressure increases more rapidly than does that of hydrocarbon fuels. This phenomenon results directly from the fact that with increases in fuel-air ratio, the moles of combustion products increases for ammonia but remains effectively insignificant for hydrocarbon fuels.

Again it should be pointed out that the results presented are based upon the assumption that ammonia can be made to burn successfully following liquid fuel injection. For this reason the predicted performance represents an upper limit to the performance one might expect to achieve in the development of Diesel engines using ammonia rather than Diesel fuel.

III) Thermal Efficiency

Figures 8 and 9 present thermal efficiencies for ammonia and for cetene. The values predicted for ammonia are somewhat higher than for hydrocarbon fuels and several features noted in the mean effective pressure results are reflected in thermal efficiency.

As shown by Figure 8 which presents efficiency as influenced by compression ratio, the efficiency for ammonia increases at a higher rate than does that for cetene, a result again of the decreasing significance of fuel vaporization with increasing compression ratio.

Figure 9 shows the influence of fuel-air ratio upon efficiency. As a consequence of the increasing moles of combustion products produced from ammonia with increasing fuel to air ratio, the efficiency of ammonia decreases less rapidly than that of cetene.

IV) Specific Fuel Consumption

In the practical evaluation of fuel performance the specific fuel consumption is more significant than thermal efficiency.

The specific fuel consumption predicted for ammonia as compared with that for cetene is given by Figures 10-12. Figure 10 shows the influence of compression ratio upon specific fuel consumption for ammonia and for cetene for a number of air-fuel ratios. Figure 11 presents specific fuel consumption as influenced by fuel-air ratio.

The specific fuel consumption of ammonia relative to that of cetene is illustrated by Figure 12. All values plotted have been normalized by assigning the value unity to the specific fuel consumption of cetene at fuel-air equivalence ratio 0.6.

It is noted that in general the specific fuel consumption to be expected with ammonia is about 2-1/2 times that to be obtained with common hydrocarbon fuels.

V) Exhaust Gas Composition

Among the more significant of the objectionable compounds present in engine exhausts is nitric oxide (NO).

At the temperatures and pressures associated with the Diesel engine combustion process, the theoretical equilibrium concentration of nitric oxide ranges to values as high as 1 percent. As the expansion process proceeds with a resultant decrease in temperature, equilibrium principles predict the decomposition of "NO" to N_2 and O_2. Therefore that concentration corresponding to the peak cycle temperature represents the maximum amount of "NO" present at any point of the cycle.

Figure 13 presents the equilibrium nitric-oxide concentration of products of combustion corresponding to the peak cycle temperature condition. Nitric oxide concentrations for ammonia are compared with those for cetene for several fuel-air ratios. It is seen that in all cases, for a given fuel-air equivalence ratio, the "NO" produced by ammonia is substantially less than that produced by cetene. It should again be pointed out that the reported values correspond to the theoretical peak cycle temperature and hence are in excess of those to be expected from the exhaust of a real engine. These values do however, indicate that "NO" concentrations, appearing in the exhaust of engines operated with ammonia should be much less than for cetene.

CONCLUSIONS

The following conclusions summarize the predicted theoretical performance of ammonia as a diesel engine fuel.

1) In the event of developments leading to successful combustion of ammonia in Diesel engine application, ammonia would be expected to yield up to 10% more power output than typical hydrocarbon fuels operating under the same conditions.

2) The thermal efficiency obtained with ammonia is predicted to range to values 20% greater than those for hydrocarbon fuels.

3) Specific fuel consumption for ammonia would be expected to be approximately 2-1/2 times greater for ammonia than for hydrocarbon fuels.

4) The exhaust concentration of NO, resulting from the use of ammonia should be substantially less than that produced by hydrocarbon fuels.

MATHEMATICAL SYMBOLS AND UNITS

T - temperature - ^{o}R

P - pressure-PSIA

V - volume - Ft^3

H - enthalpy - Btu/(lb-combustion air)

E - energy - Btu/(lb-combustion-air)

h - enthalply-Btu/mole

C_p - specific heat - at constant pressure - Btu/mole - ^{o}R

M - moles

f - mass fraction of residual gases

γ - specific heats ratio - (C_p/C_v)

X_j - mole fraction of species j

S - entropy - Btu/lb-combustion-air-^{o}R

R - universal gas constant - 1.987 $\left(\frac{Btu}{mole\text{-}^{o}R}\right)$

W - work - Btu

MEP - mean effective pressure - PSI

η_{th} - thermal efficiency

W_f - lbs fuel-per cycle

(LHV) - lower heating value of fuel - Btu/lb-fuel

Table 1. Regression Coefficients for Entropy as a Function of Energy and Volume

$$S = A + B\sqrt{E^*} + CxE^* + DxE^{*2} + FxE^{*3} + GxE^{*4} + Hx\ell n\ V + I\ x\ (\ell n\ V)^2 + J\ x\ (\ell nV)^3 + K\ x\ (\ell nV)^4 + L\ x\ (\ell nV)^5$$

Where: $E^* = E + 2000.0$ Btu, V = volume-Ft^3/lb-air, S = entropy-Btu/^oR-lb-air

Equivalence Ratio	A	B	C	D	F
0.2	$-7.087x10^{-1}$	$6.395x10^{-2}$	0	$-7.670x10^{-4}$	0
0.4	$3.256x10^{-3}$	$5.159x10^{-2}$	0	$-6.336x10^{-4}$	0
0.6	$8.947x10^{-1}$	$3.090x10^{-2}$	0	0	0
0.8	$9.656x10^{-1}$	$3.669x10^{-2}$	0	$-4.853x10^{-4}$	0
1.0	1.412	$3.448x10^{-2}$	$-1.866x10^{-2}$	0	0

Equivalence Ratio	G	H	I	J	K	L
0.2	0	$7.377x10^{-2}$	0	0	0	$-5.037x10^{-7}$
0.4	0	$7.843x10^{-2}$	0	0	0	$-5.408x10^{-7}$
0.6	$-2.229x10^{-7}$	$8.092x10^{-2}$	$1.864x10^{-3}$	0	$-9.637x10^{-4}$	$2.669x10^{-4}$
0.8	0	$8.771x10^{-2}$	$2.068x10^{-3}$	$-1.507x10^{-3}$	$2.568x10^{-4}$	0
1.0	0	$9.044x10^{-2}$	$-2.673x10^{-4}$	0	0	0

REFERENCES

1) H. K. Newhall, "Chemical Equilibrium Properties of Ammonia-Air Combustion Products", Technical Report No. 1 under contract DA-04-200-AMC-791(x) Ammonia Fuel, Army Material Command, R & D Directorate, 1964.

2) H. K. Newhall, "Calculation of Engine Performance Using Ammonia Fuel, I. Otto Cycle", Technical Report No. 2 under contract DA-04-200-AMC-791(x) Ammonia Fuel, Army Material Command, R & D Directorate, 1965.

3) "JANAF Interim Thermo Chemical Data Tables", by the Joint Army-Navy-Air Force Thermochemical Panel. ARPA Program, USAF Contract AF33(616)-6149, Thermal Laboratory, Dow Chemical Corp., Midland, Michigan, December, 1960.

Table 3. Regression Coefficients for Pressure as a Function of Energy and Entropy for Ammonia-Air Combustion Products

$$\ell n\ P = A + BxS + CxS^2 + DxS^3 + FxS^4 + GxS^5 + Hx\sqrt{E^*} + IxE^* + JxE^{*2} + KxE^{*3} + LxE^{*4}$$
$$+ Mx\sqrt{E^*}xS + NxE^*xS + OxS^2\ x\sqrt{E^*} + QxS^2\ xE^*$$

P = Pressure-psia, E^* = E+2000-Energy-Btu/lb-air, S = Entropy-Btu/lb-air-^{o}R

Equivalence Ratio	A	B	C	D	F	G	H	I
0.2	7.814	-17.58	0	0	0	3.19×10^{-2}	0.742	-6.95×10^{-3}
0.4	14.36	-16.21	0	0	0	2.39×10^{-2}	0.605	0
0.6	-0.619	-9.667	0	0	-5.06×10^{-2}	0	0.822	0
0.8	3.176	-11.46	0	0	0	0	1.227	-1.180
1.0	6.983	-8.591	0	0	-2.467×10^{-2}	0	0.938	-0.861

Equivalence Ratio	J	K	L	M	N	P	Q
0.2	0	0	0	0	0	0	9.892×10^{-3}
0.4	-5.605×10^{-3}	0	0	0	0	0	5.807×10^{-3}
0.6	-1.629×10^{-2}	0	4.143×10^{-6}	0	0	0	8.253×10^{-4}
0.8	0	1.024×10^{-4}	0	4.347×10^{-4}	0	0	0
1.0	0	0	3.349×10^{-6}	0	0	-3.961×10^{-3}	0

Table 2. Regression Coefficients for Energy as a Function of Entropy and Volume

$$E = A + BxS + CxS^2 + DxS^3 + FxS^4 + GxS^5 + Hx\ell nV + I \times (\ell nV)^2 + J \times (\ell nV)^3 + Kx(\ell nV)^4 + Lx(\ell nV)^5 + MxSx\ell nV + NxS^2x\ell nV + OxSx(\ell nV)^2 + PxS^2x(\ell nV)^2$$

S = Entropy-Btu/^{o}R-lb-air, E = Energy-Btu/lb-air, V = Volume-ft^3/lb-air

Equivalence Ratio	A	B	C	D	F	G	H
0.2	2786	289.8	0	0	0	32.96	-182.5
0.4	-2029	3093	0	0	0	-9.178	-203.4
0.6	2366	0	0	143.1	0	0	-307.2
0.8	974	0	501.6	0	0	0	-275 8
1.0	22.65	-98.82	0	0	0	18.64	0

Equivalence Ratio	I	J	K	L	M	N	O	P
0.2	252.7	8.548	0	-0.122	0	0	0	-69.18
0.4	10.95	-0.383	0.0250	0	0	0	0	0
0.6	68.47	-14.14	0	0.236	0	0	0	0
0.8	12.96	0	0	0	0	0	0	0
1.0	204.6	-31.66	0	0.350	0	-109.8	0	0

Table 5. Regression Coefficients for Volume as a Function of Enthalpy and Pressure for Ammonia-Air Combustion Products

$$V = A + Bx(H^*/P) + C \times (H^*/P)^2 + D \times (H^*/P)^3 + F \times (H^*/P)^4 + Gx(H^*/P)^5$$

V = Volume-Ft^3/lb-air, H^* = H+2000=Enthalpy-Btu/lb-air, P = Pressure-psia

Equivalence Ratio	A	B	C	D	F	G
0.2	-1.939×10^{-2}	5.916×10^{-1}	-7.656×10^{-3}	0	0	5.463×10^{-7}
0.4	3.931×10^{-2}	6.366×10^{-1}	-4.382×10^{-3}	0	0	1.983×10^{-7}
0.6	-1.131×10^{-2}	7.745×10^{-1}	-1.007×10^{-2}	0	0	1.034×10^{-6}
0.8	3.684×10^{-2}	8.428×10^{-1}	-2.659×10^{-3}	0	0	-3.768×10^{-7}
1.0	2.271×10^{-3}	1.004	-2.094×10^{-4}	0	0	0

Table 4. Regression Coefficients for Temperature as a Function of Energy and Entropy for Ammonia Combustion Products

$$T = A + Bx\sqrt{E^*} + CxE^* + DxE^{*2} + FxE^{*3} + GxE^{*4} + HxE^{*5} + IxSxE^* + JxSxE^{*2} + KxSxE^{*3} + LxSxE^{*4} + MxSxE^{*5}$$

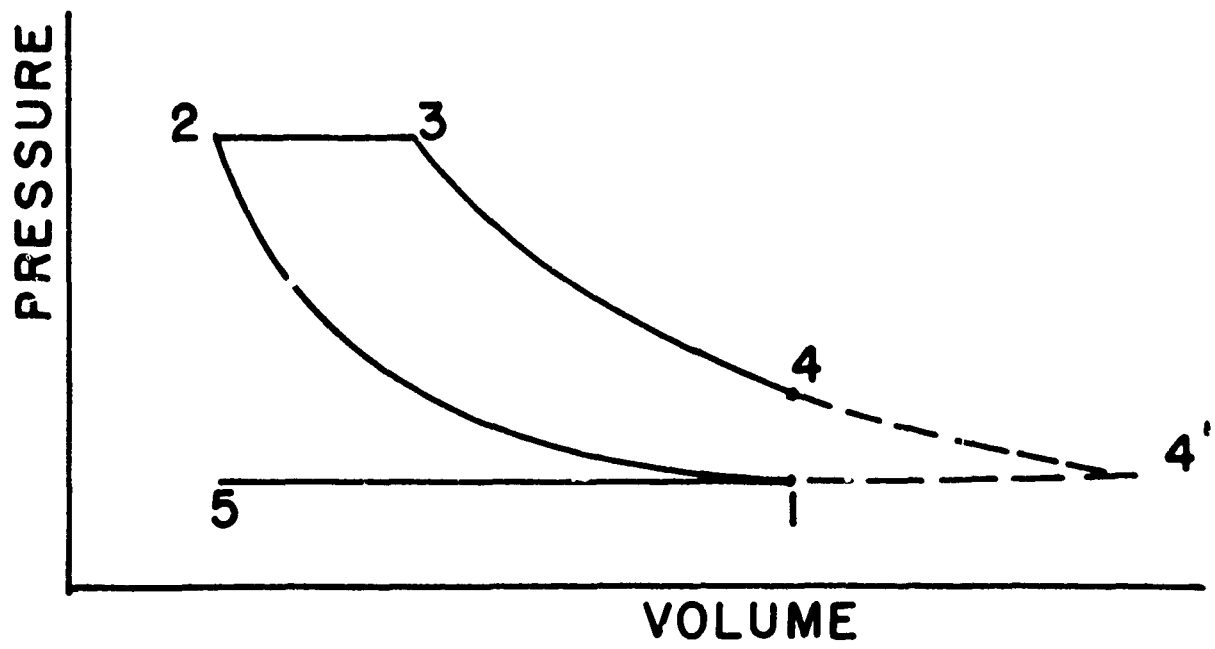
T = Temperature-^{o}R, E^* = E+2000 = Energy-Btu/lb-air, S = Entropy-Btu/^{o}R-lb air

Equivalence Ratio	A	B	C	D	F	G
0.2	-15,950	408.9	0	0	0	0
0.4	-12,510	355.1	0	0	0	0
0.6	- 9,606	311.5	0	0.126	0	0
0.8	- 6,908	262.6	0	0.903	0	0
1.0	- 5,425	247.4	0	0	0	2.079×10^{-3}

Equivalence Ratio	H	I	J	K	L	M
0.2	0	0	0	-1.921×10^{-2}	0	2.414×10^{-6}
0.4	1.018×10^{-5}	0	0	-2.069×10^{-2}	0	0
0.6	0	0	-0.593	0	0	0
0.8	0	0	-0.753	0	0	0
1.0	0	7.692	-1.399	0	0	0

FIGURE 1

THEORETICAL DIESEL CYCLE



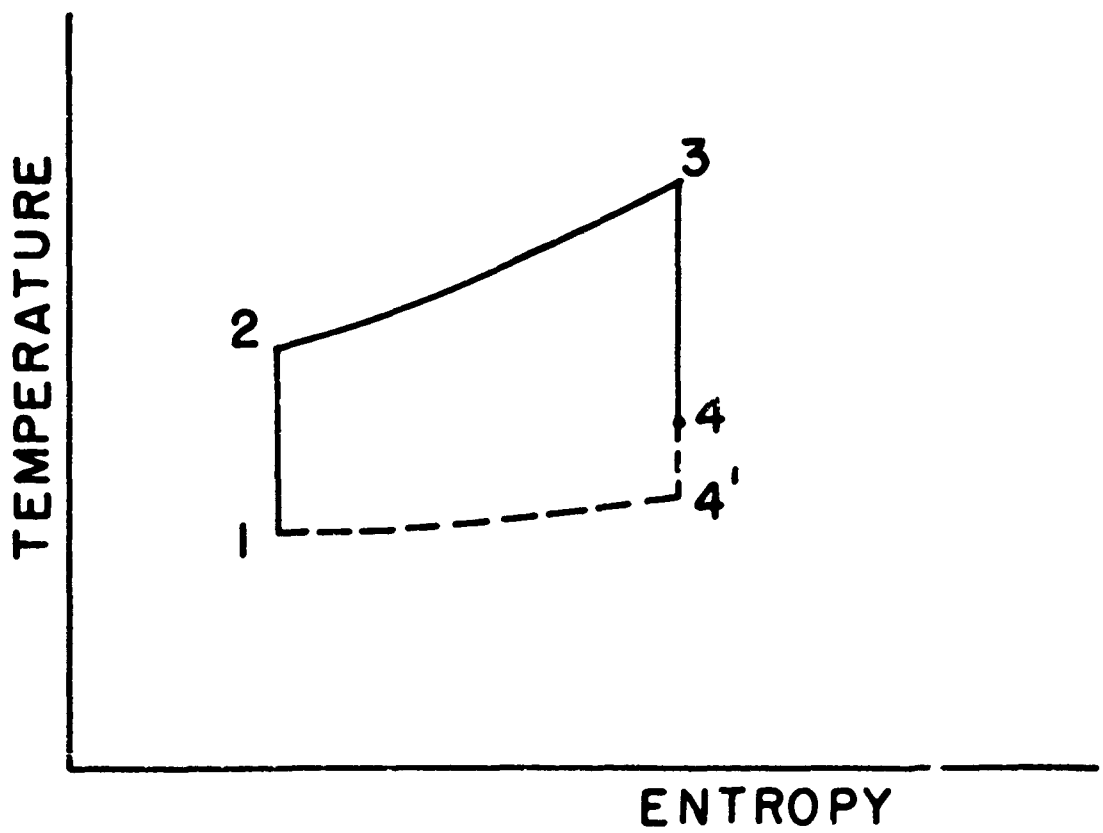


Table 6. Regression Coefficients for Temperature as a Function of Entropy at Atmospheric Pressure for Ammonia-Air Combustion Products

$$T = A + BxS + CxS^2 + DxS^3 + ExS^4 + FxS^5$$

T = Temperature-^{o}R, S = Entropy-Btu/^{o}R-lb-air

Equivalence Ratio	A	B	C	D	E	F
0.2	3838	-2719	0	0	0	90.05
0.4	3526	-2362	0	0	0	64.16
0.6	3068	-1985	0	0	0	47.82
0.8	987.5	0	-438.7	0	0	37.88
1.0	2537	-1503	0	0	0	26.80

FIGURE 2

INFLUENCE OF FUEL-AIR RATIO UPON PEAK CYCLE TEMPERATURE

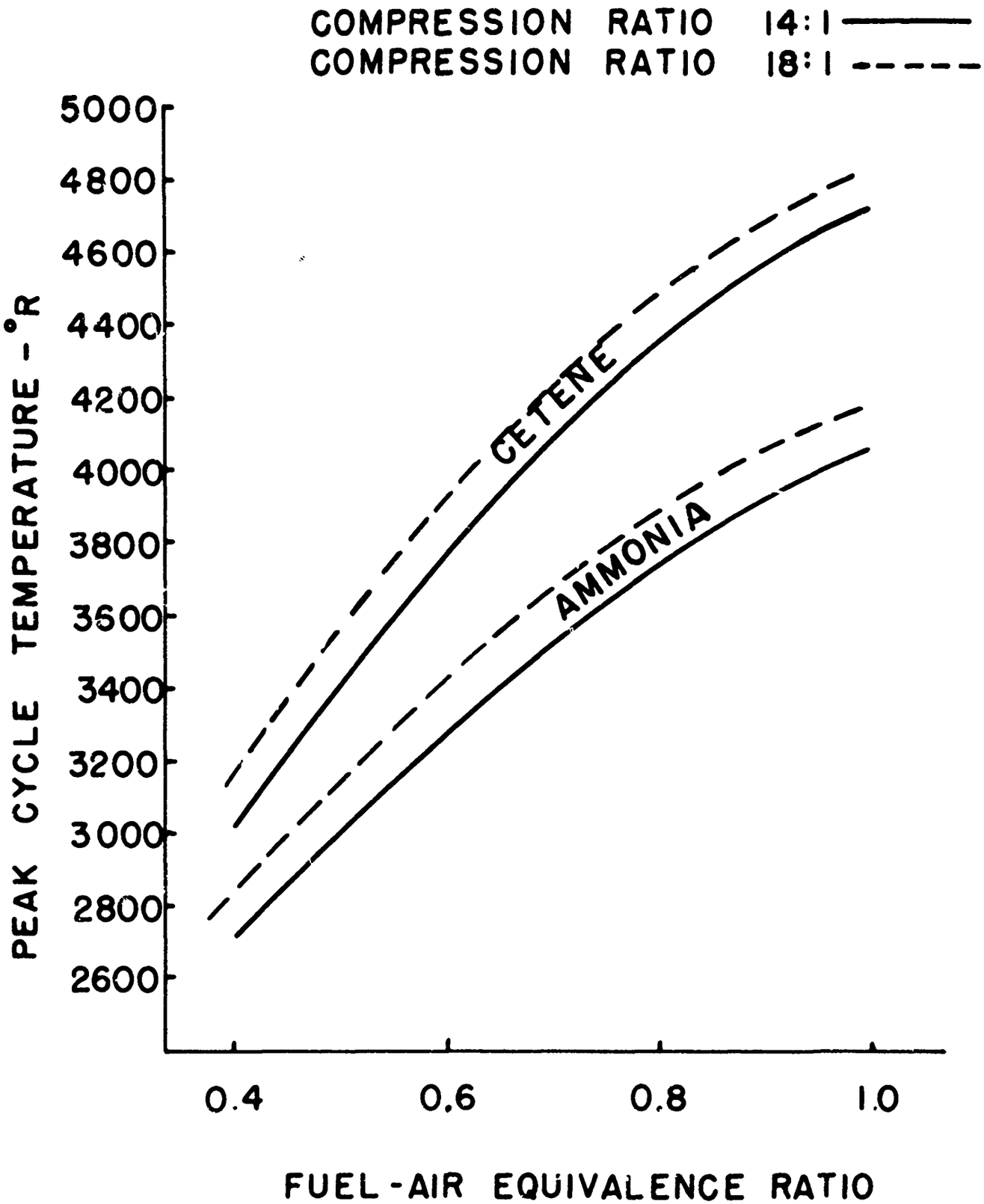


FIGURE 3

INFLUENCE OF COMPRESSION RATIO UPON PEAK THEORETICAL CYCLE TEMPERATURE

FUEL-AIR EQUIVALENCE RATIO 0.6

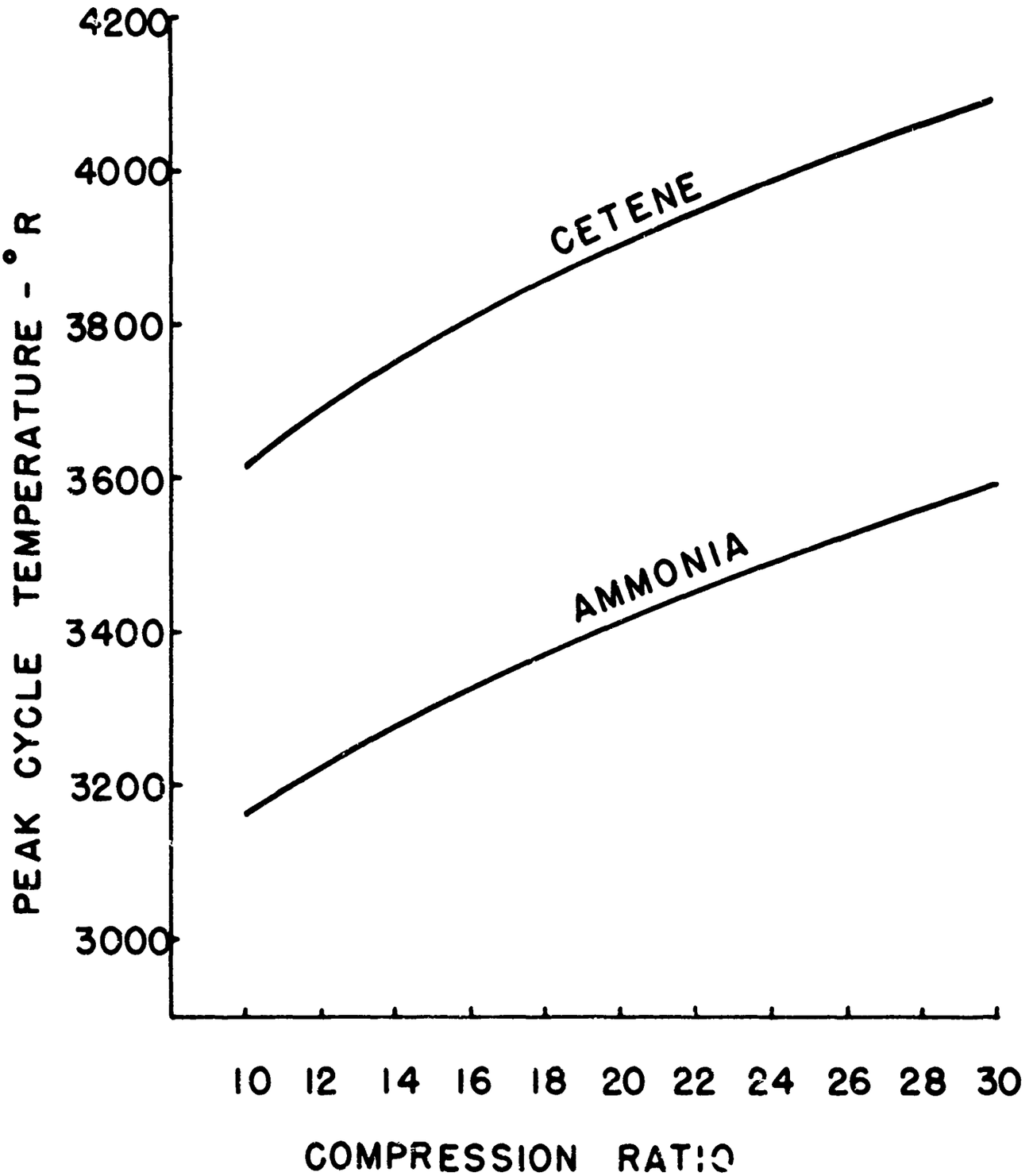


FIGURE 4

INFLUENCE OF COMPRESSION RATIO UPON THEORETICALLY PREDICTED PEAK CYCLE PRESSURE

FUEL-AIR EQUIVALENCE RATIO 0.6

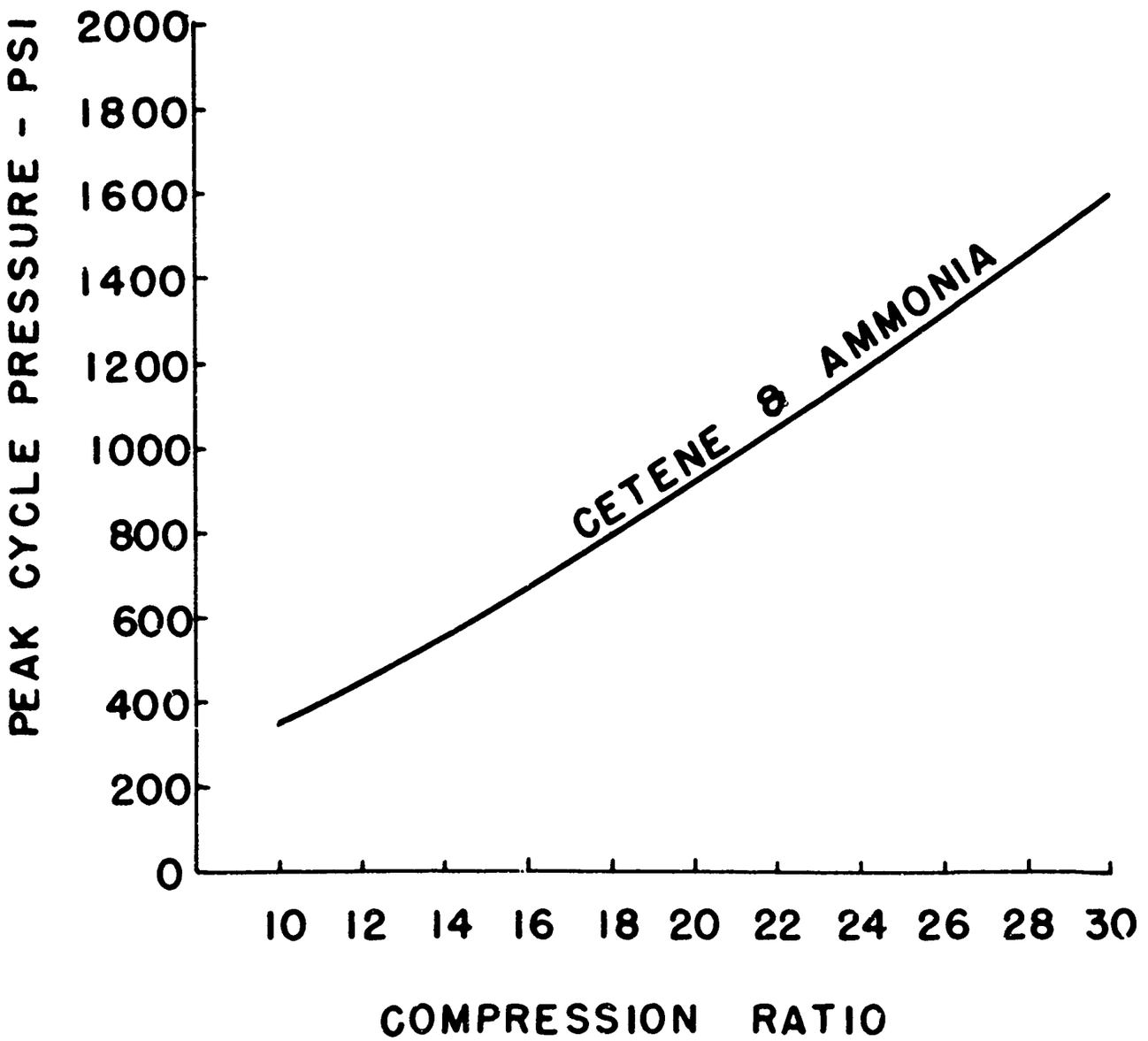


FIGURE 5

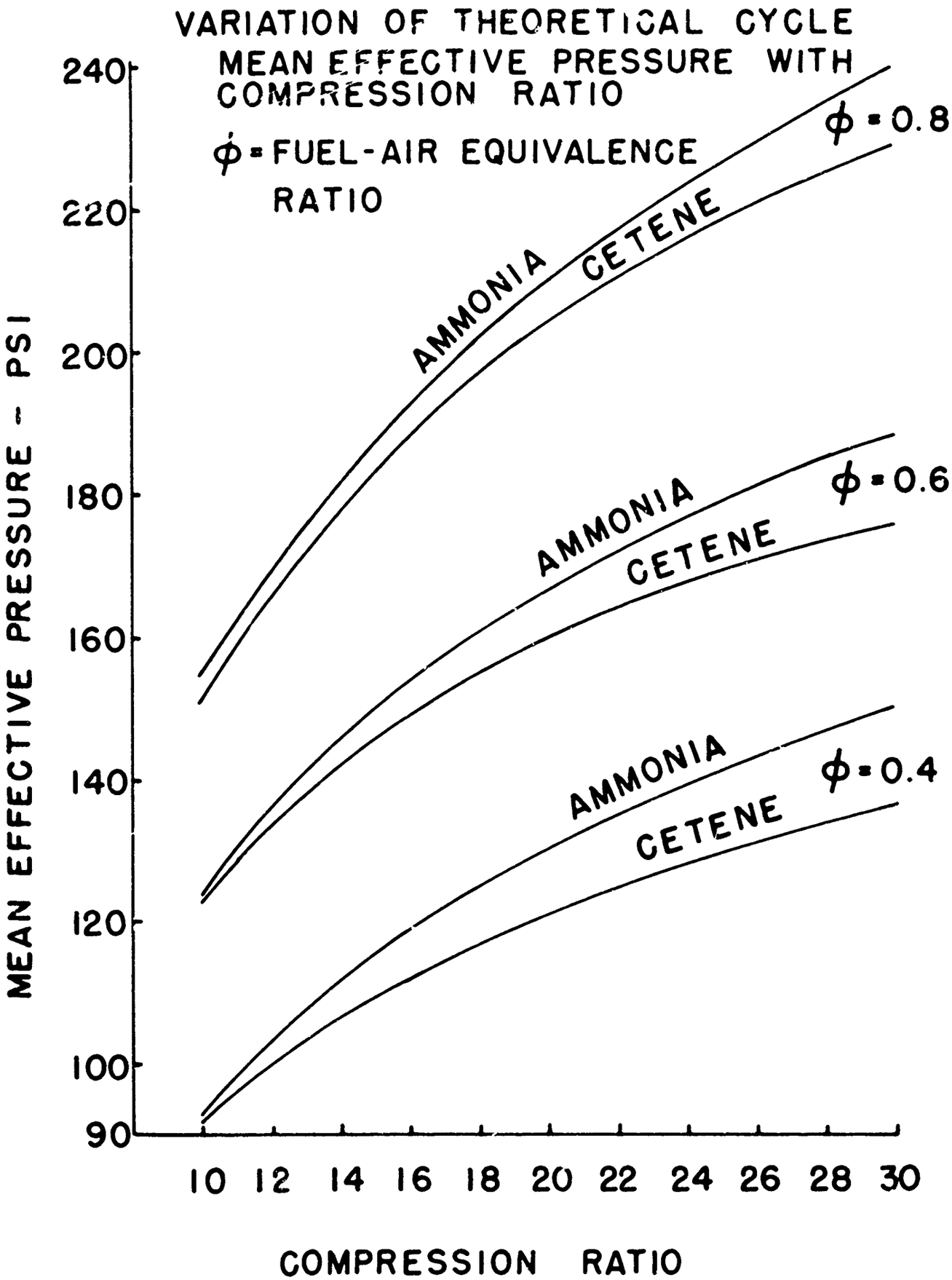

VARIATION OF THEORETICAL CYCLE MEAN EFFECTIVE PRESSURE WITH COMPRESSION RATIO
ϕ = FUEL-AIR EQUIVALENCE RATIO
ϕ = 0.8
AMMONIA
CETENE
ϕ = 0.6
AMMONIA
CETENE
ϕ = 0.4
AMMONIA
CETENE
MEAN EFFECTIVE PRESSURE - PSI
240
220
200
180
160
140
120
100
90
10 12 14 16 18 20 22 24 26 28 30
COMPRESSION RATIO

FIGURE 8

MEAN EFFECTIVE PRESSURE OF AMMONIA AND CETENE RELATIVE TO CETENE AT $\phi = 0.6$

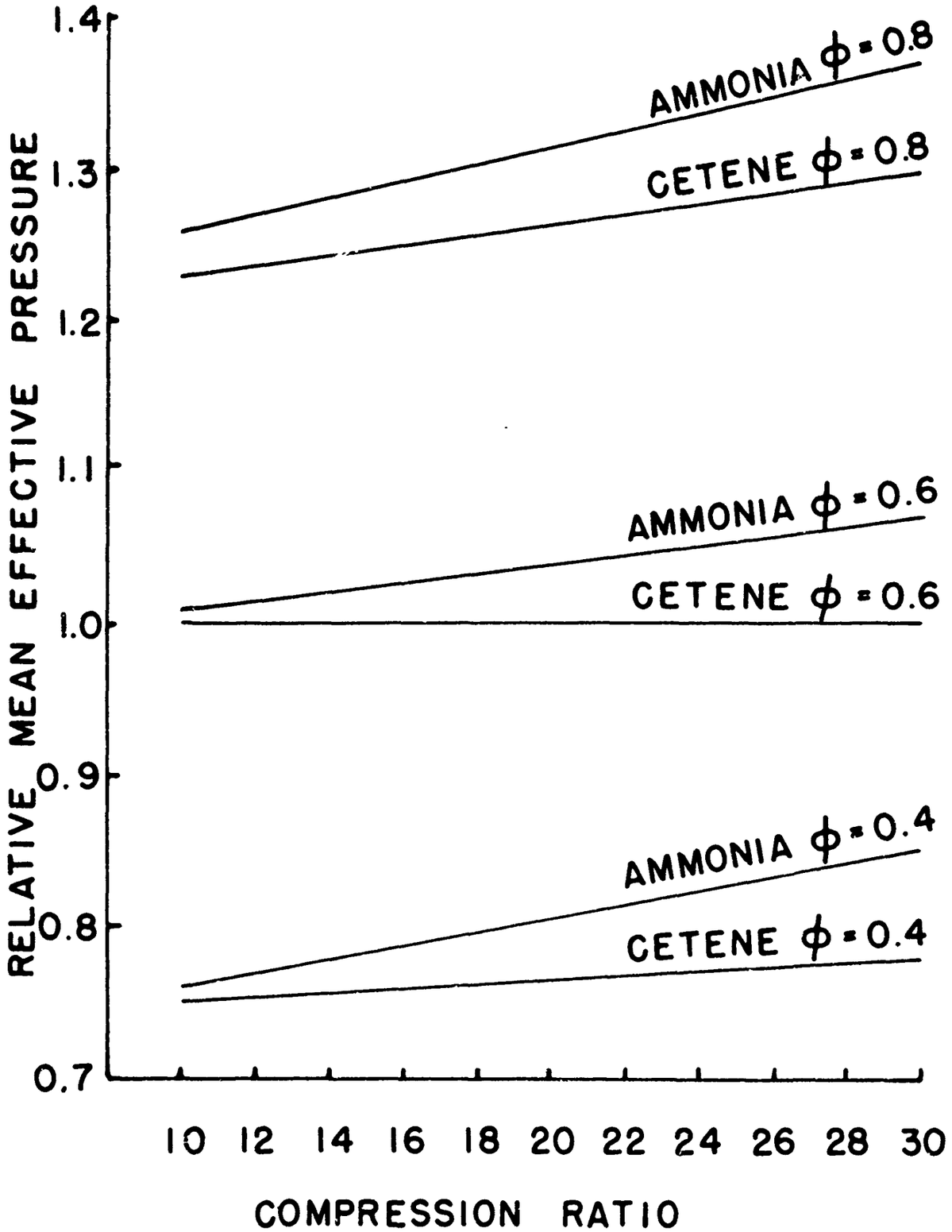


FIGURE 7

VARIATION OF THEORETICAL CYCLE MEAN EFFECTIVE PRESSURE WITH FUEL-AIR RATIO

COMPRESSION RATIO 14:1

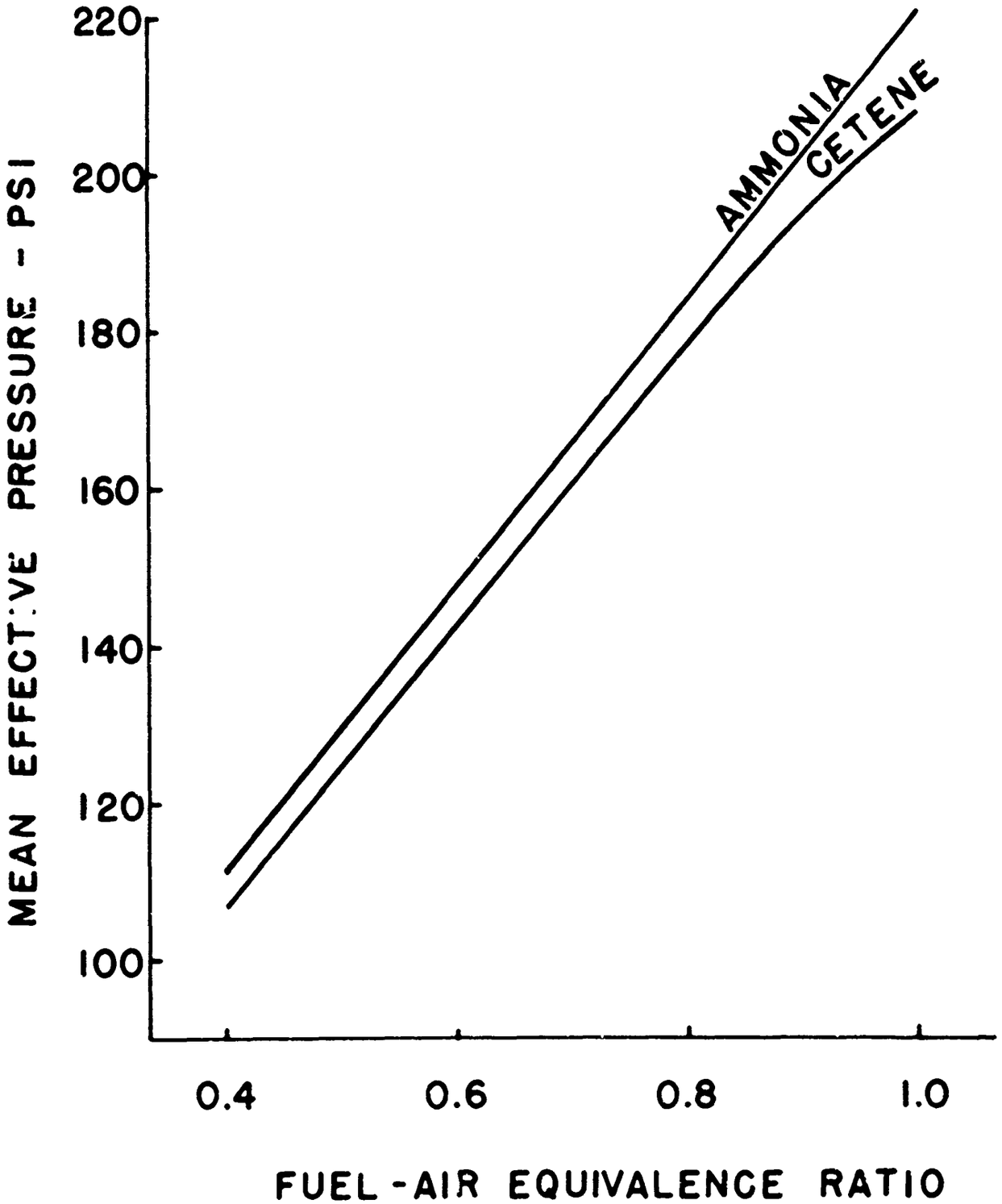


FIGURE 8

VARIATION OF THEORETICAL THERMAL EFFICIENCY WITH COMPRESSION RATIO

FUEL-AIR EQUIVALENCE RATIO 0.6

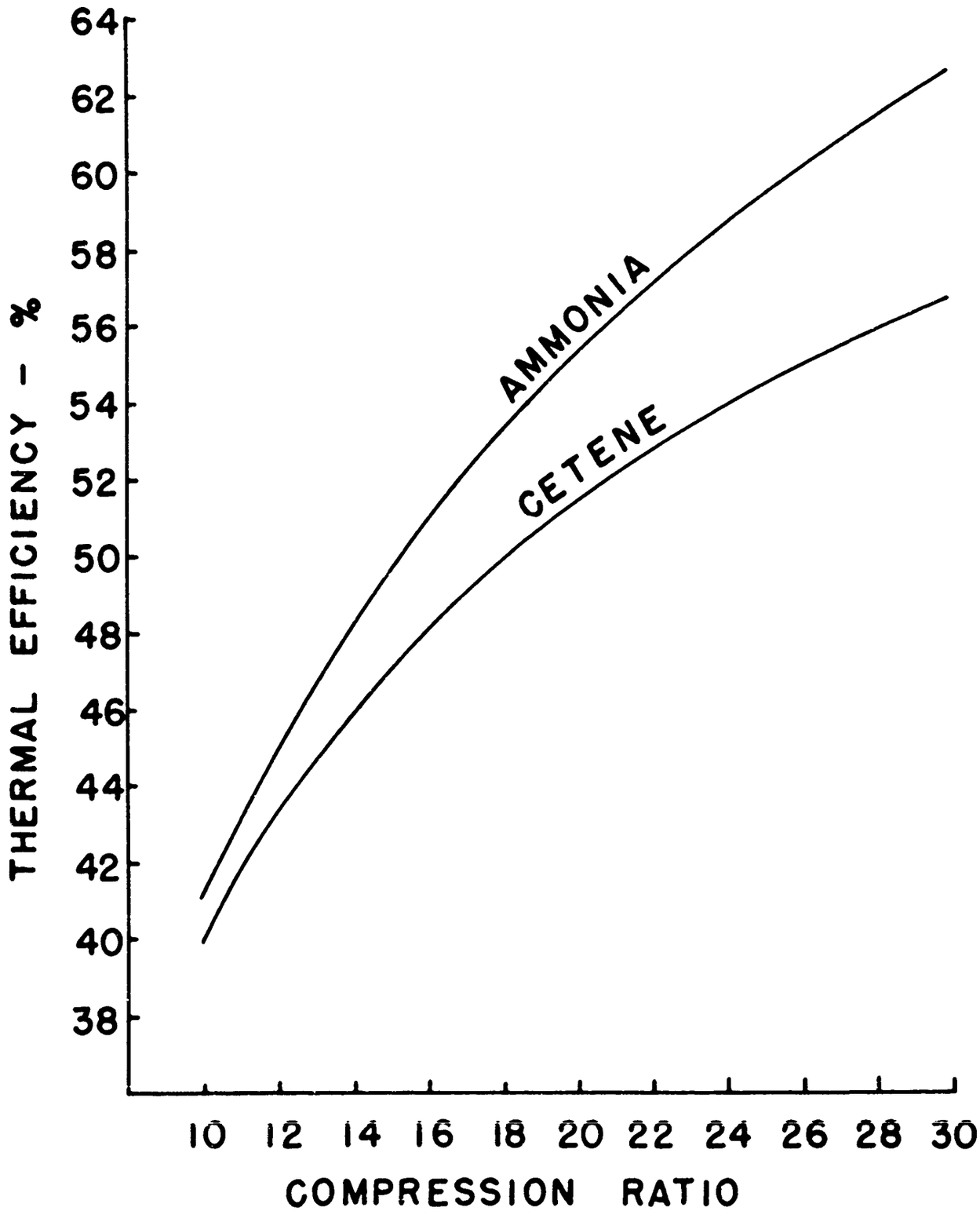


FIGURE 9

VARIATION OF THEORETICAL THERMAL EFFICIENCY WITH FUEL-AIR RATIO

COMPRESSION RATIO 16 : 1

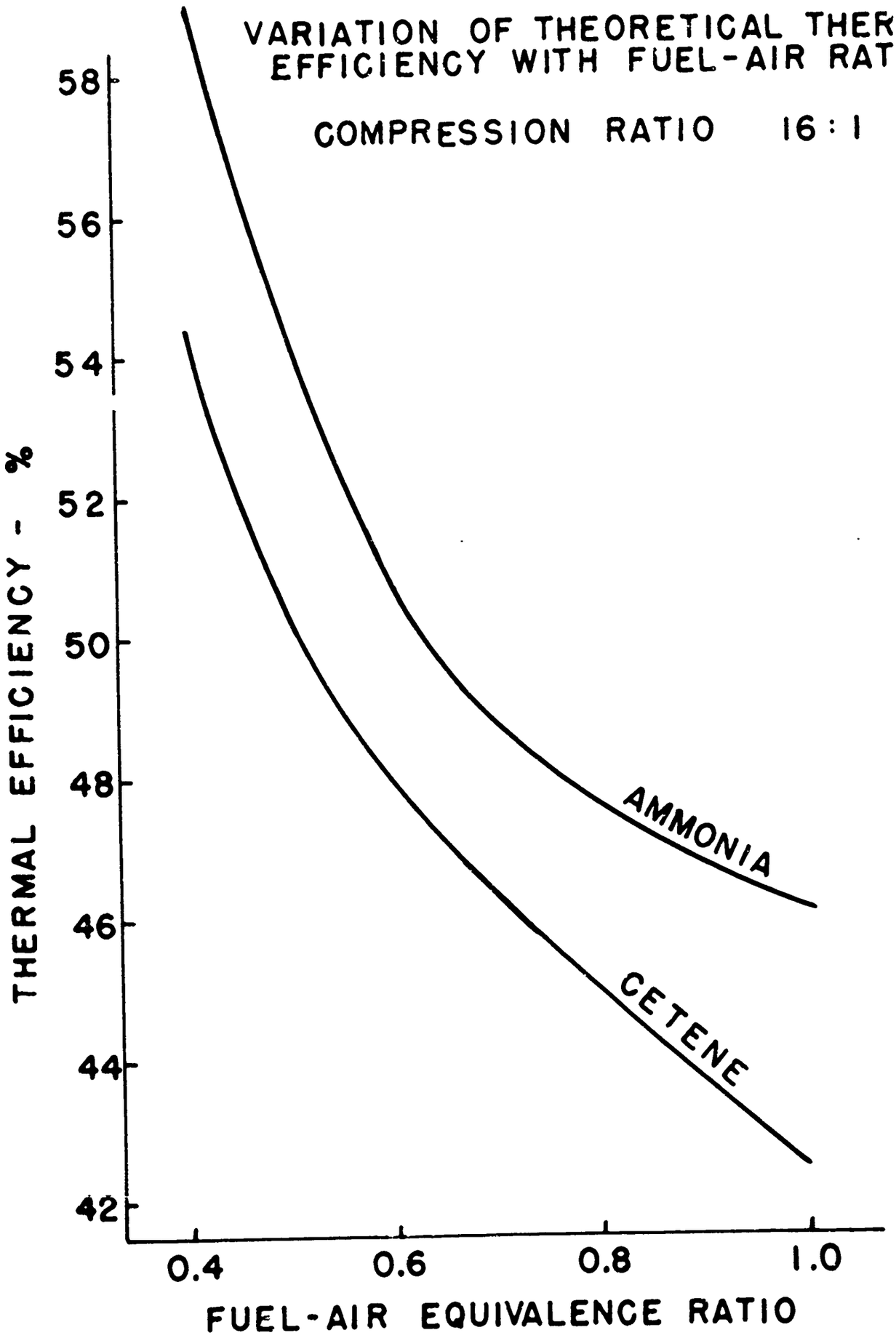


FIGURE 10

THEORETICAL SPECIFIC FUEL CONSUMPTION AS INFLUENCED BY COMPRESSION RATIO

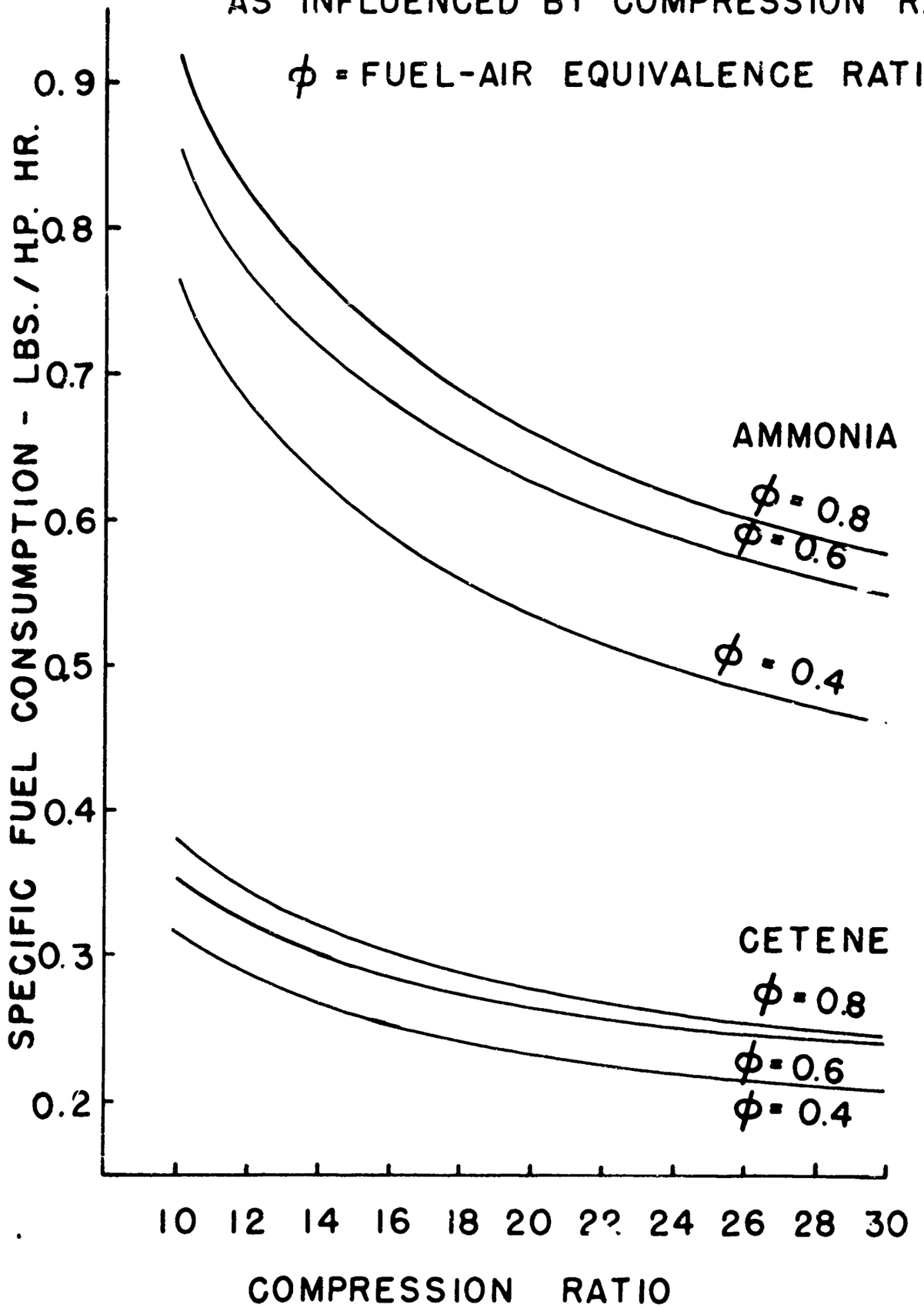


FIGURE 11

VARIATION OF THEORETICAL SPECIFIC FUEL CONSUMPTION WITH FUEL-AIR RATIO

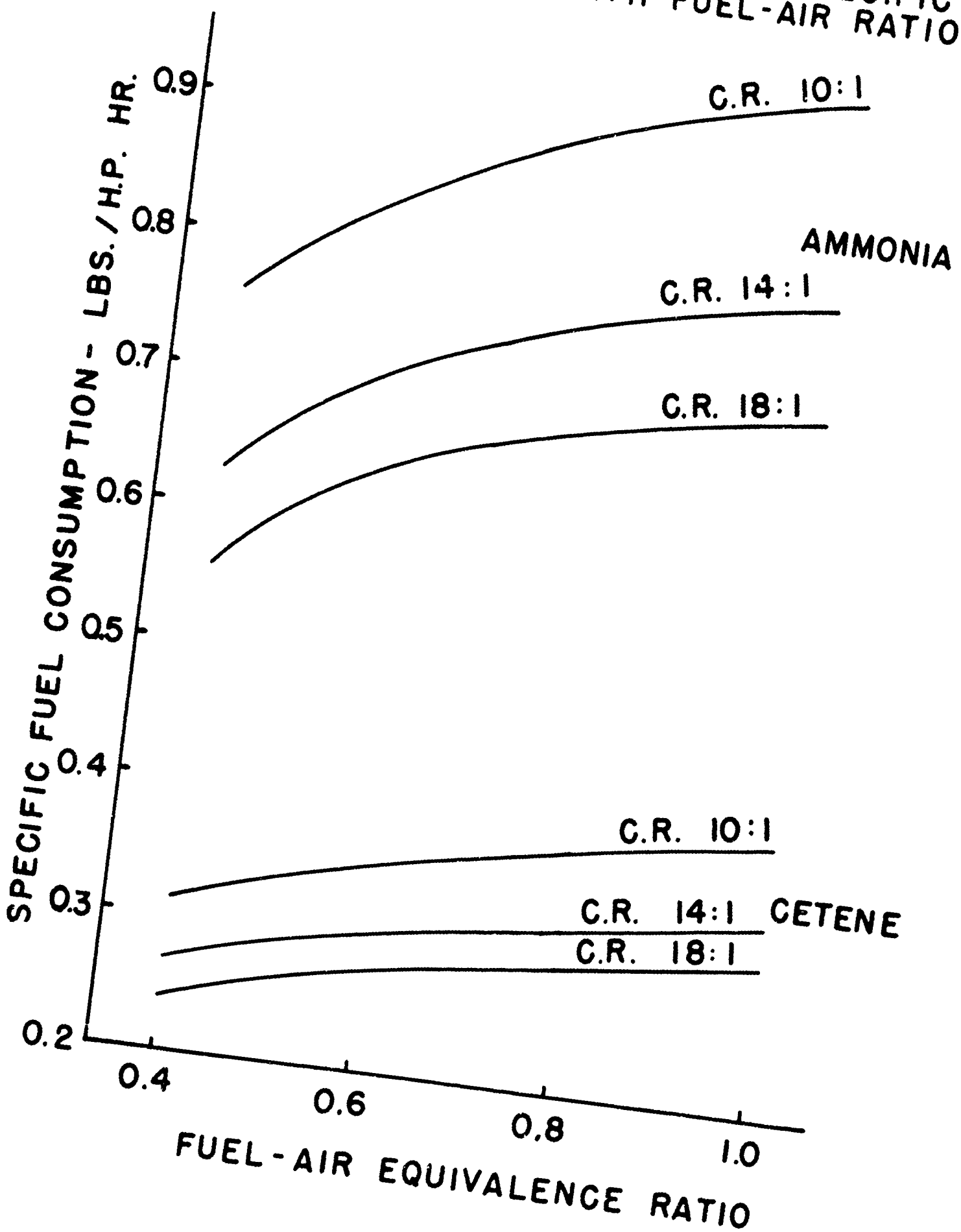


FIGURE 12

THEORETICAL SPECIFIC FUEL CONSUMPTION RELATIVE TO THAT OF CETENE AT $\phi = 0.6$

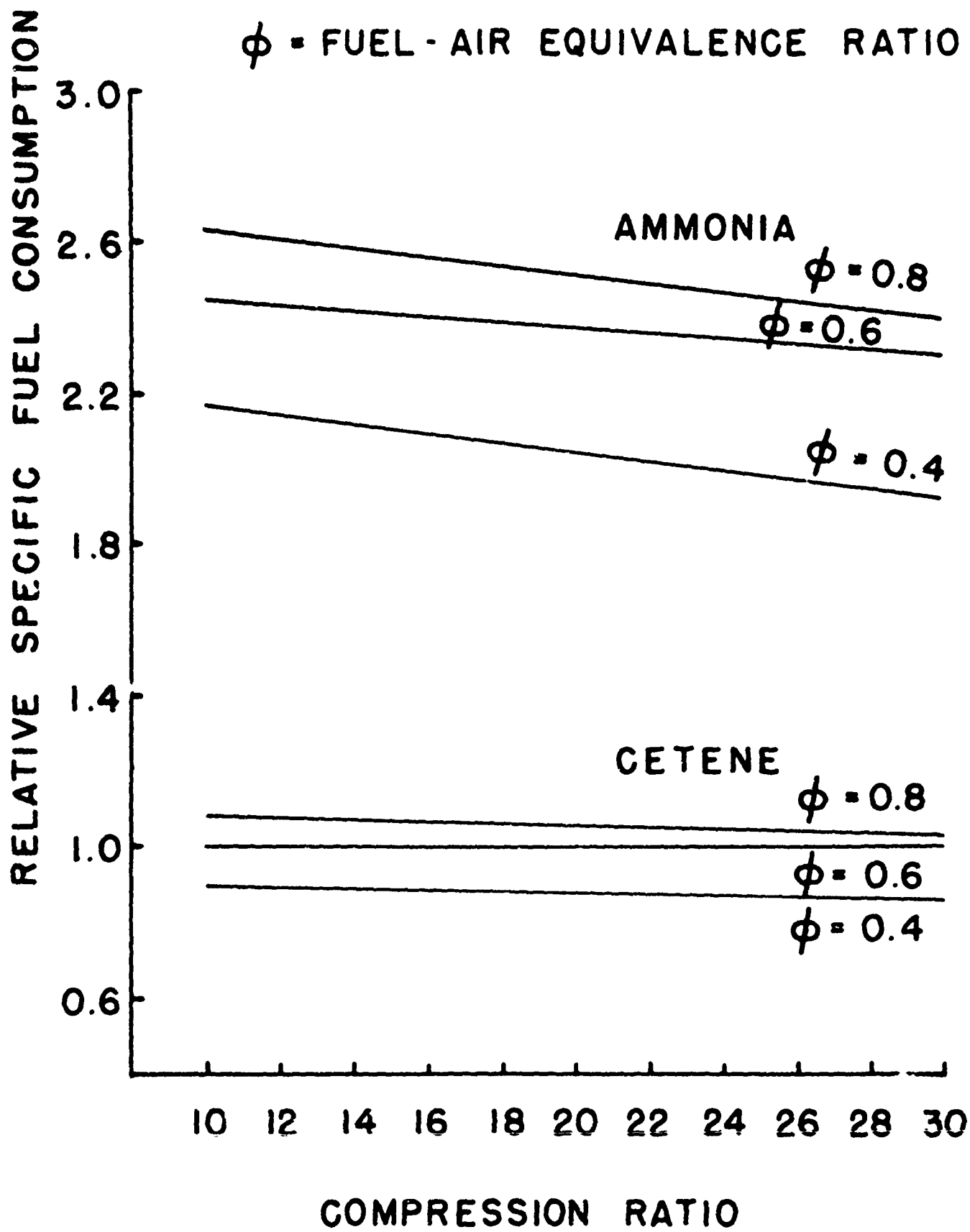


FIGURE 13

THEORETICAL EQUILIBRIUM NITRIC OXIDE CONCENTRATION AT PEAK THEORETICAL CYLINDER TEMPERATURE

ϕ = FUEL-AIR EQUIVALENCE RATIO

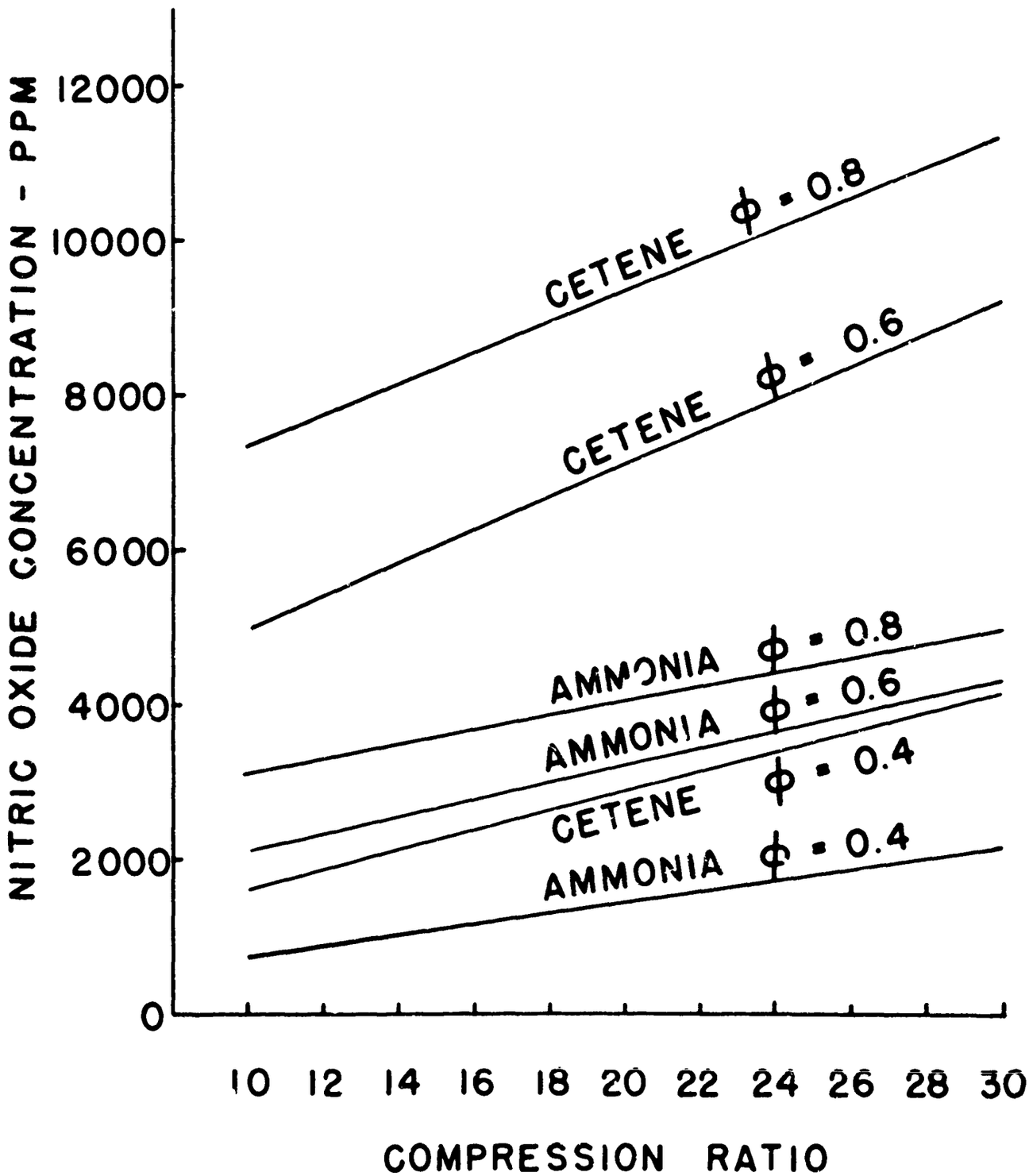
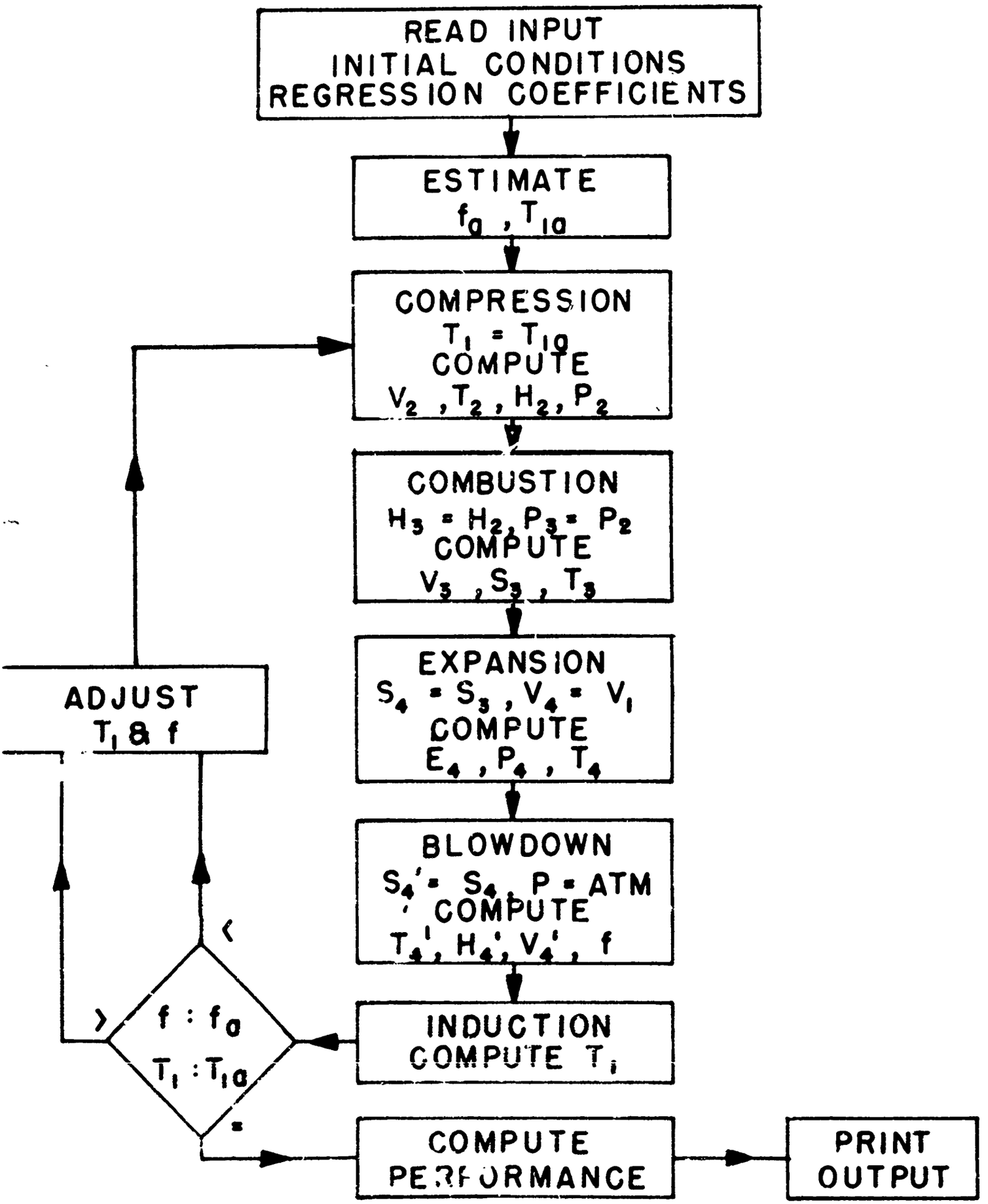



FIGURE 14
DIESEL CYCLE PROGRAM