



Thermodynamic Properties of Unburned Reactant Mixtures for Different Kind of Fuels

Hasan Kayhan KAYADELEN

Yıldız Teknik Üniversitesi, Gemi İnşaatı ve Denizcilik Fakültesi, Türkiye
hkayhan@yildiz.edu.tr, ORCID ID: orcid.org/0000-0003-4292-3770

Abstract

Accurate estimation of adiabatic flame temperature and combustion product species play a key role in estimating performance and emission characteristics of internal combustion engines. This can be succeeded only with exact knowledge of temperature and thermodynamic properties of the unburned mixture. In this paper, thermodynamic properties of various fuels and fuel-air mixtures are presented. Differences in gas phase and liquid phase properties are discussed. Effect of equivalence ratio and unburned mixture temperature on enthalpy, specific heat and entropy of unburned fuel-air mixtures as well as effect of phase change on adiabatic flame temperature are shown. In order to serve as a recourse tool for researchers of combustion and internal combustion engines, the required polynomial coefficients used in calculation of thermodynamic properties are tabulated in famous NASA format for various important chemical compounds which are commonly used to represent surrogates of diesel, gasoline, Jet-A and many other fuels.

Keywords: Combustion, Fuels, Unburned Mixture, Thermodynamic Properties, NASA Format.

Farklı Yakıtlara Ait Yanmamış Dolgu Karışımlarının Termodinamik Özelliklerinin Belirlenmesi

Öz

İçten yanmalı motorlarda yanma ürünleri ve adyabatik alev sıcaklığının hassas bir şekilde tayin edilmesi, performans ve kirletici emisyonların doğru olarak hesaplanabilmesinde önemli bir rol oynamaktadır. Bu da ancak yanmamış dolguya ait termodinamik özelliklerin tam olarak bilinmesiyle mümkündür. Bu çalışmada çeşitli yakıt ve yakıt-hava karışımlarının, ayrıca bunlarla birlikte bulunan diğer reaktanların varlığında termodinamik özelliklerin tayin edilebilmesi için hassas sonuç veren bir metot tanıtılmış, yakıtların sıvı veya gaz fazında bulunmaları halinde termodinamik özellikler ve adyabatik alev sıcaklığında meydana gelen değişimler incelenmiştir. Bahsedilen metot kullanılarak diesel, benzin, ve jet-A gibi yakıtları oluşturan ve sıkça kullanılan yakıt bileşenlerinin sıvı hallerindeki termodinamik özelliklerinin hesaplanmasında kullanılacak katsayılar, yaygın olarak kullanılan NASA formatında hesaplanarak tablolaştırılmış, içten yanmalı motorlar üzerine çalışan araştırmacıların istifadesine sunulmuştur.

Anahtar Kelimeler: Yanma, Yakıtlar, Yanmamış Dolgu, Termodinamik Özellikler, NASA Polinomları.

1. Introduction

Improving cycle parameters such as thermal efficiency and work produced by an engine or reducing exhaust gas emissions are the main objectives of many studies on energy systems [1-4]. In order to calculate these cycle parameters precisely, we need an accurate computation of the changes of state due to combustion. Fuel-air mixtures are usually composed of more than one thermodynamic phase. Accordingly, rather than modeling the fuel-air mixture as an ideal gas mixture, a more realistic approach is to regard each individual species in their actual phases [5]. This task can be performed in two different ways, one of which is to provide the properties of the substances in a tabular form at predetermined temperature intervals and the values needed are calculated by interpolation. This method requires, handling thousands of thermodynamic values, large memory storage and does not permit use beyond the temperature limits of the table. A second and more commonly used technique is representation of the properties of each species by polynomials that allow direct calculation of the thermodynamic properties at any temperature. The polynomials obtained from fitting specific heat, entropy and enthalpy with simultaneous least squaring of are known as the NASA thermodynamic polynomials because of their use in a variety of NASA computer programs [6]. The NASA polynomials are usually fitted in the temperature range 300 to 5000 K one is for 300 to 1000 K and the other is from 1000 to 5000 K range [7]. Because the scope of this work is unburned mixture properties, polynomial coefficients of low temperature range (300 to 1000 K) is of concern.

Numerous researches of internal combustion engines and gas turbines [8-17] use these polynomial coefficients in performance calculations which calculate thermodynamic properties matching that

of famous combustion software CHEMKIN [18] and of Gaseq [19]. In most cases, these coefficients for individual substances can only be found for gas phase but gas phase polynomial coefficients cannot represent thermodynamic properties at liquid phase. Accordingly, direct usage of gas phase coefficients for calculation of unburned mixture properties cause deviations in thermodynamic properties which deteriorate performance parameters such as net cycle work, thermal efficiency and energy efficiency, and also parameters that affect pollutant emissions such as adiabatic flame temperature and the combustion products. For instance, according to [20] the thermal NO_x production rate doubles for every 90 K temperature increase beyond 2100 K.

In this study, a method presented in authors previous work [21] is used for calculation of polynomial coefficients for liquid fuels from the available ideal gas thermodynamic coefficients taken from [22]. Precision of presented liquid phase polynomial coefficients are improved. To show the reliability of the method, a comparison is made with polynomial coefficients which are directly derived from the actual liquid phase thermodynamic properties taken from the thermodynamic tables of NIST obtained from their renown software Refprop [23]. Calculation procedure of the unburned mixture temperature and mixture thermodynamic properties are presented for different fuel/air ratios and fuel compositions allowing any reactant species to be included in the unburned mixture. The required liquid phase polynomial coefficients for 14 most frequently used chemical compounds such as methanol, ethanol, isooctane, toluene, which represent surrogates of diesel, gasoline jet-A and other frequently used liquid fuels are tabulated in famous NASA format to provide a reference for researchers of combustion and internal

combustion engines. Effects of equivalence ratio and unburned mixture temperature on enthalpy, specific heat and entropy of unburned fuel-air mixtures as well as effects of phase change on adiabatic flame temperature are presented showing that correct determination of the polynomial coefficients is substantial to obtain thermodynamic properties, flame temperature and accordingly exhaust species accurately which would improve the precision of any thermo-economic and thermo-environmental model.

2. Theoretical Model

Equations (1)-(3) give molar specific heat, enthalpy and entropy respectively for each individual species i in the reactant mixture. $a_{1,i}$ - $a_{7,i}$ are the so called NASA polynomial coefficients of each species which are given in Table 2.

$$\frac{\bar{c}_{p,i}}{R_u} = a_{1,i} + a_{2,i} T + a_{3,i} T^2 + a_{4,i} T^3 + a_{5,i} T^4 \quad [kJ/mol] \quad (1)$$

$$\frac{\bar{h}_i}{R_u T} = a_{1,i} + \frac{a_{2,i}}{2} T + \frac{a_{3,i}}{3} T^2 + \frac{a_{4,i}}{4} T^3 + \frac{a_{5,i}}{5} T^4 + \frac{a_{6,i}}{T} \quad [kJ/mol] \quad (2)$$

$$\frac{\bar{s}_i^o}{R_u} = a_{1,i} \ln T + a_{2,i} T + \frac{a_{3,i}}{2} T^2 + \frac{a_{4,i}}{3} T^3 + \frac{a_{5,i}}{4} T^4 + a_{7,i} \quad [kJ/mol] \quad (3)$$

where \bar{R}_u is the molar universal gas constant equal to 8.31434 kJ/kmol K defined as $R_u = R_i M_i$ where M_i denotes the molecular weight of the unburned reactant. After obtaining the thermodynamic values for each species i , thermodynamic properties of unburned fuel-air mixture at a certain temperature can be calculated according to the molar ratios y_i as below:

Here, y_i stands for the mole fractions of four constituents of air (O_2 , N_2 , H_2O and Ar) and fractions of constituents of fuel if composed of more than one species. If present, any additional reactant species can be included in Eqs. (4)-(6). When the equivalence ratio is known, fuel and air mass ratios can be obtained as follows:

$$\phi = FA/FA_s \quad (7)$$

Here, FA is the fuel-air ratio and FA_s is the stoichiometric fuel-air ratio of the fuel. After obtaining the specific heats of air and fuel separately, temperature of the unburned fuel mixture can be calculated as follows:

$$T_u = \left[T_{fuel} C_{p,fuel} m_{fuel} + T_{air} C_{p,air} m_{air} \right] / \left[C_{p,fuel} m_f + C_{p,air} m_{air} \right] \quad (8)$$

Here, T_{fuel} is fuel temperature, $C_{p,fuel}$ is the fuel constant pressure specific heat, m_{fuel} is the mass of fuel, m_{air} is the amount of total combustion air, and $C_{p,air}$ is the constant pressure specific heat corresponding to T_{air} . If additional species exist, it should be included in Eq. (8) just as fuel and air.

For an arbitrarily selected liquid fuel toluene, thermodynamic properties obtained from Refprop are given in Figure 1. The validation of Refprop data and reference states given to Refprop are done using Gaseq unburned results at dedicated temperature and pressure. The pressure entered in Gaseq is the pressure given by Refprop 0,10577 atm at an arbitrarily selected temperature of 320 K. At this pressure and temperature, Gaseq gives the enthalpy as 568,18 kJ/kg matches well with that of NIST Refprop, 567,28 kJ/kg, shown in Figure 1.

$$c_{p,u} = m_{air} c_{p,air} + m_{fuel} c_{p,fuel} = m_{air} \left(\frac{1}{M_{air}} \sum_{i=1}^4 y_i \bar{c}_{p,i} \right) + m_{fuel} \left(\sum_{i=1}^n \frac{y_i \bar{c}_{p,i}}{M_i} \right) \quad [kJ/kg] \quad (4)$$

$$h_u = m_{air} h_{air} + m_{fuel} h_{fuel} = m_{air} \left(\frac{1}{M_{air}} \sum_{i=1}^4 y_i \bar{h}_i \right) + m_{fuel} \left(\sum_{i=1}^n \frac{y_i \bar{h}_i}{M_i} \right) \quad [kJ/kg] \quad (5)$$

$$s_u = m_{air} s_{air} + m_{fuel} s_{fuel} = m_{air} \left(\frac{1}{M_{air}} \sum_{i=1}^4 y_i \bar{s}_i \right) + m_{fuel} \left(\sum_{i=1}^n \frac{y_i \bar{s}_i}{M_i} \right) \quad [kJ/kg] \quad (6)$$

2: toluene: Saturation points (at equilibrium)

	Temperature (K)	Pressure (atm)	Liquid Enthalpy (kJ/kg)	Vapor Enthalpy (kJ/kg)	Liquid Entropy (kJ/kg-K)	Vapor Entropy (kJ/kg-K)	Liquid Cp (kJ/kg-K)	Vapor Cp (kJ/kg-K)	Heat of Vapor. (kJ/kg)	Molar Mass
1	273,15	0,0089127	87,331	515,47	0,98853	2,5560	1,6254	1,0286	428,14	92,138
2	290,00	0,024213	115,13	533,21	1,0873	2,5289	1,6751	1,0975	418,08	92,138
3	320,00	0,10577	166,82	567,28	1,2568	2,5082	1,7720	1,2219	400,46	92,138
4	340,00	0,23850	202,96	591,61	1,3663	2,5094	1,8413	1,3065	388,65	92,138
5	360,00	0,48362	240,52	617,10	1,4735	2,5196	1,9136	1,3925	376,58	92,138
6	380,00	0,89896	279,57	643,60	1,5789	2,5369	1,9886	1,4803	364,04	92,138
7	383,40	0,99140	286,36	648,20	1,5966	2,5404	2,0016	1,4955	361,84	92,138

Figure 1. Output of REFPROP for Thermodynamic Properties of Toluene at Dedicated Temperatures and Reference States

However, entropy of Refprop, 2,5082 kJ/kg K, verified from Goodwin [24] seems inconsistent that of Gaseq, 3,75706 kJ/kg K. This is because entropy of Gaseq given at 320 K and 0,10577 atm is for ideal gas phase and therefore needs the following correction given by Eq.(9) according to the equation of Gibbs for liquid state entropy at equilibrium state and the heat of vaporization at corresponding temperature:

$$s_{liq} = s_{gas@0,10577atm} - \Delta h_{vap} / T = 3,75706 - 400,46 / 320 = 2,506 \quad [kJ/kgK] \quad (9)$$

$$h_{liq} = h_{gas} - \Delta h_{vap} = 568,18 - 400,46 = 167,72 \quad [kJ/kg] \quad (10)$$

Heat of vaporization in Eq. (9) and Eq. (10) can be calculated with Eq. (11) using the coefficients C₁-C₄ and reduced temperature T_r=T/T_c. Here, T is the temperature in Kelvin and T_c is critical temperature taken from [25]. C₃ and C₄ are equal to zero for the fuels investigated. Other variables used in Eq. (11) are tabulated in Table 1.

$$\Delta h_{vap} = C_1 (1 - T_r)^{c_2 + c_3 T_r + c_4 T_r^2} \quad (11)$$

In thermodynamics, the absolute values of enthalpy, entropy, and energy at a single state point are meaningless. It is only the difference between two different state points matters. Thus, the value for a single state point can be set to any arbitrary value.

Many handbooks set the arbitrary state point so that the values of these properties are positive for most liquid or gas states. The properties of enthalpy and entropy are computed as differences relative to some arbitrary reference state [26]. In this study, the liquid phase reference state enthalpies and entropies given to Refprop are set exactly to their values at 298,15 K and 1 bar which are calculated by substituting gas phase enthalpy and entropy values

at 298,15 K and 1 bar into Eqs. (9)-(10). Gas phase enthalpy and entropy values at 298,15 K and 1 bar are obtained with Gaseq software using gas phase thermodynamic coefficients a₁-a₇ for T=300-100K given in Table 2. Calculated liquid phase reference enthalpy and entropy values, which are used to obtain properties from Refprop relative to NASA reference states, are presented in Table 1.

Comparison of Table 3 and Table 4 show that enthalpy and entropy values calculated by Refprop according to the reference enthalpy and entropy data given in Table 1 can safely be used in obtaining liquid phase polynomial coefficients and will successfully represent the thermodynamic

Table 1. Parameters for Vaporization Enthalpy Equation and Reference Values for Enthalpy and Entropy Obtained from the Calculated Liquid Phase a_1 - a_7 Coefficients at 298,15 K and 1 bar

	C_1	C_2	T_c	h_{liq} kJ/kg	h_{gas} kJ/kg	S_{liq} kJ/kgK	S_{gas} kJ/kgK	$\Delta h_{vap-REFPROP}$
Toluene	49,507	0,37742	591,75	129,84	542,69	2,0883	3,4730	412,85
n-Decane	66,126	0,39797	617,7	-2114,76	-1753,72	2,6249	3,8358	361,04
Benzene	45,346	0,39053	689	627,76	1061,32	1,9950	3,4492	433,56
n-Pentane	39,109	0,38681	469,7	-2477,25	-2210,96	3,9075	5,1360	366,29
Methanol	50,451	0,33594	512,5	-7445,03	-6276,03	3,5617	7,4825	1169
Hexane	44,544	0,39002	507,6	-2302,9	-1937,43	3,2859	4,5117	365,47

properties in consistency with Gaseq.

Properties of all fuels presented in Table 4 are obtained from the calculated liquid phase polynomial coefficients a_1 - a_7 . To obtain liquid phase polynomial coefficients, enthalpy values at 6 evenly distributed temperature in the range of 273,15 K to T_{sat} are taken from Table 3 which presents the liquid phase thermodynamic properties calculated with Refprop. These enthalpy values are used to solve the equation: $k \times A = B$ for k to obtain a_1 - a_6 where

$$A = \begin{bmatrix} 1 & T_1/2 & T_1^2/3 & T_1^3/4 & T_1^4/5 & 1/T_1 \\ 1 & T_2/2 & T_2^2/3 & T_2^3/4 & T_2^4/5 & 1/T_2 \\ 1 & T_3/2 & T_3^2/3 & T_3^3/4 & T_3^4/5 & 1/T_3 \\ 1 & T_4/2 & T_4^2/3 & T_4^3/4 & T_4^4/5 & 1/T_4 \\ 1 & T_5/2 & T_5^2/3 & T_5^3/4 & T_5^4/5 & 1/T_5 \\ 1 & T_6/2 & T_6^2/3 & T_6^3/4 & T_6^4/5 & 1/T_6 \end{bmatrix} \quad B = \begin{bmatrix} h_1 / (RT_1) \\ h_2 / (RT_1) \\ h_3 / (RT_1) \\ h_4 / (RT_1) \\ h_5 / (RT_1) \\ h_6 / (RT_1) \end{bmatrix} \quad k = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{bmatrix} \quad (12)$$

and h in kJ/kg. To obtain a_7 , Eq. (8) is used. As there is only one unknown, one temperature value is enough to solve a_7 from Eq. (13) below:

$$a_7 = - \left[a_1 \log(T_1) + a_2 T_1 + a_3 T_1^2 / 2 + a_4 T_1^3 / 3 + a_5 T_1^4 / 4 \right] - \frac{s_1}{R} \quad (13)$$

where s_1 is the liquid phase entropy at temperature T_1 . Using unburned mixture enthalpy, adiabatic flame temperature can be obtained minimizing ΔT as follows:

$$\Delta T = (h_u - h_v) / C_p \quad (14)$$

Here h_u is the total enthalpy of reactants, h_b is the enthalpy of the products and C_p is the specific heat of the burnt gas. Burned gas properties are calculated according to the chemical equilibrium method proposed by [6] and [27] considering 10 product species. Iteratively, adiabatic flame temperature is obtained by:

$$AFT^{n+1} = AFT^n + \Delta T \quad (15)$$

For each iteration (n), h_u , h_b and C_p are reevaluated until ΔT becomes less than

an acceptable tolerance which is taken as 10^{-5} in this study.

3. Results and Discussion

In order to determine liquid phase polynomial coefficients for toluene, n-decane, benzene, n-pentane and methanol and hexane, the actual enthalpy are entropy values taken from Refprop which are presented in Table 3. These values are obtained using the liquid phase reference states given in Table 1. Ideal gas thermodynamic data for low temperature (300-1000 K) [22] and calculated liquid

phase data are presented in Table 2. To validate the obtained liquid phase thermodynamic data, thermodynamic properties are calculated using Eqs. (1)-(3) using the obtained liquid phase data given

in Table 2. The values are presented in Table 4. Refprop values given in Table 3 and calculated values given in Table 4 are very close with an average absolute deviation in enthalpy |0.0011%|, entropy |0.0061%|

Table 2. Calculated Liquid Phase Coefficients a_1 - a_7 , from Results of REFPROP for 273,15 K to the Saturation Temperature at 1 bar and Gas Phase Coefficients for 300 to 1000 K

Fuels	T (K)	a_1	a_2	a_3	a_4	a_5	a_6	a_7
CH ₃ OH	273-T _{sat}	-646,7031	8,515793	-0,04147624	8,96586E-05	-7,23619E-08	9022,0516	2353,7397
	300-1000	2,660115	0,007342	7,17005E-06	-8,79319E-09	2,39057E-12	-25353,48	11,23263
C ₂ H ₅ OH	273-T _{sat}	-699,9972	9,176359	-0,04476726	9,76705E-05	-7,98241E-08	7602,1751	2553,734835
	300-1000	0,1791061	0,030906	-1,936E-05	6,31831E-09	-8,53167E-13	-29567,061	24,47159
C ₅ H ₁₂	273-T _{sat}	156639	-2165,53	11,2226243	-0,025836427	2,22945E-05	-9084275	-561380
	300-1000	10,04976	-0,019352	1,4755E-04	-1,69026E-07	6,289703E-11	-21454,04	-12,12254
C ₆ H ₆	283-T _{sat}	391,2617	-4,75421	0,02240288	-4,67099E-05	3,65755E-08	-22325,22	-1448,37
	300-1000	-3,13801	0,04723	-0,0296E-04	-0,03263E-06	1,71869E-11	8890,031	36,57573
C ₆ H ₁₄	273-T _{sat}	-3959,3863	51,551371	-0,250134802	0,000538815	-4,34379E-07	215399,833	14438,617
	300-1000	1,836174	0,0509846	1,2596E-05	-4,42836E-08	1,872237E-11	-22927,49	20,88145
C ₇ H ₈	273-T _{sat}	13,04711	0,02703	-0,00016714	6,89549E-07	-7,17719E-10	-3199,95	-56,5045
	300-1000	-2,53688	0,052899	1,4039E-06	-4,07623E-08	2,037752E-11	4477,848	37,41512
C ₇ H ₁₆	273-T _{sat}	62,87312	0,00066	-0,00202554	8,56744E-06	-9,62659E-09	-44656,880	-303,351
	300-1000	11,1533	-0,009494	1,9557E-04	-2,49754E-07	9,848777E-11	-26768,89	-15,90968
C ₈ H ₁₈	273-T _{sat}	138,4995	-1,39505	0,006389919	-1,26202E-05	9,42853E-09	-45321,297	-530,156
	300-1000	1,1759	0,073227	1,1217E-05	-5,564996E-08	2,463636E-11	-28667,47	22,36527
C ₉ H ₁₂	273-T _{sat}	10,59797	-2,64E-06	0,000262034	-4,98291E-07	3,98255E-10	-9294,742	-38,485
	300-1000	4,674885	0,019894	1,25511-04	-1,817844E-07	7,472863E-11	-2122,436	11,830198
C ₁₀ H ₈	273-T _{sat}	8,819087	1,36E-05	0,000280991	-5,16720E-07	3,43067E-10	7122,5606	-40,2164
	300-1000	-1,049195	0,046297	7,07592E-05	-1,38408E-07	6,204754E-11	15984,9	30,21216
C ₁₀ H ₁₄	273-T _{sat}	9,904477	-8,87E-06	0,000286849	-4,93461E-07	3,56033E-10	2333,7534	-37,1121
	300-1000	5,029490	0,006937	2,0424E-04	-2,79971E-07	1,138555E-10	9970,859	10,68859
C ₁₀ H ₂₂	273-T _{sat}	7182,861	-93,4367	0,456722542	-0,00098965	8,02635E-07	-482873,58	-26164,3
	300-1000	15,43282	-0,013298	2,82481E-04	-3,65923E-07	1,45372E-10	-35863,28	-27,94543
C ₁₁ H ₁₀	273-T _{sat}	9,422619	1,14E-05	0,00028288876	-4,85268E-07	3,00461E-10	17030,125	-37,9392
	300-1000	1,591975	0,034402	1,24038E-04	-2,01416E-07	8,67316E-11	25890,536	23,75374
C ₁₆ H ₃₄	273-T _{sat}	23,7035	8,87E-05	0,000653645	-1,28346E-06	8,86626E-10	-65348,85	-90,7578
	300-1000	-2,281474	0,185128	-9,9178E-05	1,433984E-08	3,732305E-12	-51744,93	56,00249
N ₂	300-1000	3,298677	0,001408	-0,0396E-04	0,056415E-07	-0,02445E-10	-1020,900	3,950372
O ₂	300-1000	3,212936	0,001128	-5,7562E-07	1,313877E-09	-8,76855E-13	-1005,249	6,034737
H ₂ O	300-1000	3,386842	0,003475	-6,3547E-06	6,96858E-09	-2,50659E-12	-30208,11	2,590232
Ar	300-1000	2,5	0	0	0	0	-745,375	4,366

and specific heat |0.3918%|. The absolute average deviation is |0.133%|. Further, comparison of Table 3 and Table 4 shows that liquid and ideal gas thermodynamic coefficients are well interchangeable

temperature limit) and ended with the saturation temperature of each fuel at 1 bar.

Figure 2 shows the variation of enthalpy of unburned fuel-air mixture with equivalence ratios changing between

Table 3. NIST Refprop Liquid Phase Thermodynamic Data for Toluene, n-Decane, Benzene, n-Pentane, Methanol and Hexane

Toluene				n-Decane			
T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK	T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK
273,15	1,6257	88,269	1,9423	273,15	2,1040	-2168,5	2,4369
290	1,6757	116,08	2,0410	290	2,1628	-2132,6	2,5645
320	1,7731	167,79	2,2106	305	2,2183	-2099,7	2,6750
340	1,8425	203,95	2,3202	320	2,2760	-2065,9	2,7829
360	1,9145	241,54	2,4275	335	2,3356	-2031,4	2,8885
380	1,9889	280,60	2,5329	345	2,3762	-2007,8	2,9578
383,4	2,0018	287,39	2,5506	347,3	2,3856	-2002,3	2,9736
Benzene				n-Pentane			
T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK	T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK
283,15	1,698	602,01	1,9064	273,15	2,2099	-2503,8	3,7097
290	1,7144	613,70	1,9472	280	2,2371	-2488,6	3,7647
305	1,754	639,71	2,0346	290	2,2791	-2466,0	3,8439
320	1,7977	666,36	2,1198	295	2,3011	-2454,5	3,8830
335	1,8446	693,69	2,2032	300	2,3239	-2443,0	3,9218
350	1,8941	721,75	2,2850	305	2,3473	-2431,3	3,9604
353,1	1,9046	727,64	2,3017	308,2	2,3626	-2423,7	3,9850
Methanol				Hexane			
T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK	T [K]	C _p kJ/kgK	h kJ/kg	s kJ/kgK
273,15	2,4011	-7506,7	3,3460	273,15	2,1525	-2357,9	3,0932
285	2,4593	-7477,9	3,4491	285	2,1982	-2332,2	3,1856
300	2,5461	-7440,3	3,5774	300	2,2598	-2298,7	3,2999
310	2,6120	-7414,5	3,6619	310	2,3032	-2275,9	3,3746
325	2,7223	-7374,5	3,7878	320	2,3482	-2252,6	3,4484
335	2,8034	-7346,9	3,8715	330	2,3949	-2228,9	3,5213
336,8	2,8186	-7341,8	3,8866	340,8	2,4472	-2202,7	3,5992

as one can be converted to the other if vaporization enthalpies are known at each temperature step at which the polynomials are interpolated.

Temperatures in Table 3 and Table 4 are started from 0°C (except for benzene because of the Refprop's minimum

0.3 and 1.4 and for unburned mixture temperatures of 300, 500, 700 and 900 Kelvin. According to Figure 2, enthalpy increases almost linearly with unburned mixture temperature. Among the 10 fuels investigated, methanol mixture shows the highest enthalpy change at all temperatures

Table 4. Calculated with the Calculated a_1 - a_7 Data

Toluene				n-Decane			
T [K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK	T[K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK
273,15	1,6259	88,270	1,9423	273,15	2,1166	-2168,5	2,4369
290	1,6758	116,081	2,0411	290	2,1591	-2132,6	2,5644
320	1,7736	167,792	2,2107	305	2,2264	-2099,7	2,6750
340	1,8433	203,952	2,3202	320	2,2771	-2065,9	2,7832
360	1,9161	241,542	2,4277	335	2,3272	-2031,4	2,8886
380	1,9902	280,605	2,5332	345	2,3941	-2007,8	2,9579
383,4	2,0029	287,393	2,5510	347,3	2,4174	-2002,3	2,4369
Benzene				n-Pentane			
T [K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK	T [K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK
283,15	1,6992	602,020	1,9064	273,15	2,2519	-2503,84	3,7098
290	1,7145	613,710	1,9472	280	2,2189	-2488,64	3,7647
305	1,7547	639,721	2,0347	290	2,2950	-2466,04	3,844
320	1,7991	666,371	2,1200	295	2,3012	-2454,54	3,8833
335	1,8454	693,702	2,2034	300	2,3018	-2443,04	3,922
350	1,8964	721,756	2,2853	305	2,3569	-2431,43	3,9604
353,1	1,9080	727,652	2,3021	308,2	2,4647	-2423,74	3,9855
Methanol				Hexane			
T [K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK	T [K]	C_p kJ/kgK	h kJ/kg	s kJ/kgK
273,15	2,3928	-7506,747	3,3459	273,15	2,1249	-2357,92	3,0934
285	2,4652	-7477,947	3,4491	285	2,2035	-2332,22	3,1854
300	2,5491	-7440,346	3,5776	300	2,2608	-2298,72	3,3000
310	2,6124	-7414,546	3,6622	310	2,3006	-2275,92	3,3747
325	2,7239	-7374,546	3,7882	320	2,3493	-2252,68	3,4485
335	2,8041	-7346,906	3,8720	330	2,4019	-2228,92	3,5216
336,8	2,8183	-7341,846	3,8870	340,8	2,4456	-2202,72	3,5998

followed by syngas, ethanol, dimethyl ether (dme) and methane mixtures. For $T_u=300$ K, enthalpy of methanol decreases by 303% when equivalence ratio is increased from 0.3 to 1.4. For fuel-air mixtures with surrogates of diesel, gasoline, jet-A and also for isooctane and propane, effect of equivalence ratio on the mixture enthalpy is negligible. For example at 900 K enthalpy of gasoline is 647 kJ/kg at $\Phi=0.3$ and 672.4 kJ/kg at $\Phi=1.4$. However, the net effect of temperature change on the enthalpies of diesel, gasoline, jet-A and propane are

almost the same.

Figure 3 shows the variation of entropy of unburned fuel-air mixture with equivalence ratios changing between 0.3 and 1.4 and for unburned mixture temperatures of 300, 500, 700 and 900 Kelvin. According to Figure 3, entropy increases almost linearly with unburned mixture temperature as for enthalpy. It can be seen from the figure that, for the same fuel, variation of entropy with equivalence ratio is almost parallel to each other. Among the 10 fuels investigated, syngas-air mixture shows the highest

Table 5. Liquid Fuel Surrogates Representing Jet-A, Diesel and Gasoline

		Surrogates			Syngas [28]
		Jet A [29]	Diesel [30]	Gasoline [31]	
Carbon monoxide	CO	Fuel molar mixture			0,5
Hydrogen	H ₂				0,5
Isooctane	C ₈ H ₁₈		0,33		0,34
Toluene	C ₇ H ₈		0,243		
n-Pentane	C ₅ H ₁₂				0,10
Benzene	C ₆ H ₆				0,56
α-methylnaphthalene(MNP)	C ₁₁ H ₁₀			0,30	
n-Decane	C ₁₀ H ₂₂		0,427	0,70	

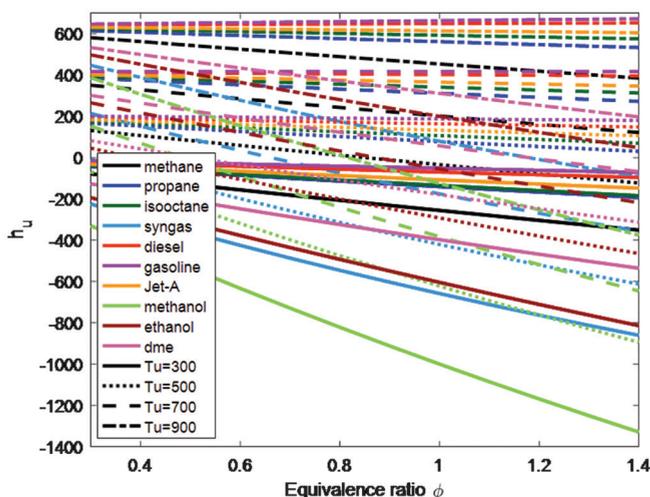


Figure 2. Enthalpy of Unburned Fuel-Air Mixture for Various Fuels at Different Equivalence Ratios and for Different Unburned Mixture Temperatures

entropy change with equivalence ratio at all temperatures followed by methane and methanol mixtures. For unburned mixture temperature of 300 K, entropy increases by 12.2% for syngas and by 5% for methane when equivalence ratio is increased from 0.3 to 1.4. For these mixtures, entropy increases with equivalence ratio. For, diesel, gasoline, jet-A, propane, ethanol, isooctane and dme mixtures, entropy values are very close to each other and slightly decrease with equivalence ratio.

Figure 4 shows the variation of specific heat of unburned fuel-air mixture with

equivalence ratios changing between 0.3 and 1.4 and for unburned mixture temperatures of 300, 500, 700 and 900 Kelvin. According to Figure 4, specific heat increases linearly with equivalence ratio for each fuel-air mixture. It can be seen from the figure that, for the same fuel, variation of specific heats with equivalence ratio are parallel to each other for unburned temperatures of 300 K, 500 K, 700 K and 900 K as it was in Figure 2 and Figure 3 except for the case that the fuels are methanol, ethanol at 300 K where both fuels are in their liquid phase. Highest specific

heat values are for methanol, ethanol, dme, methane and isooctane respectively for gas phase whereas in liquid phase specific heat is highest for methanol, syngas and ethanol which has a significantly higher specific heat than its successors isooctane, methane, jet-A and diesel. According to Figure 4, lowest specific heats are for propane and dme at 300 K.

Figure 5 shows the change of adiabatic flame temperatures of unburned fuel-air mixture for varying equivalence ratios at 300 K unburned mixture temperature. Unburned properties are calculated with gaseous polynomial coefficients and with calculated liquid fuel coefficients adiabatic flame temperatures are presented comparatively. This is a substantial

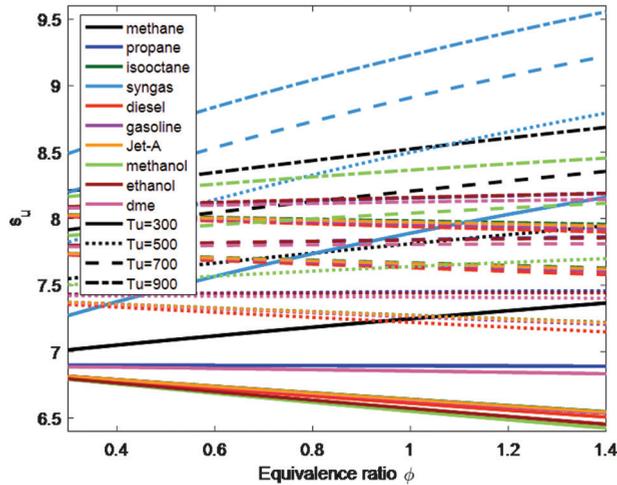


Figure 3. Entropy of Unburned Fuel-Air Mixture for Various Fuels at Different Equivalence Ratios and for Different Unburned Mixture Temperatures

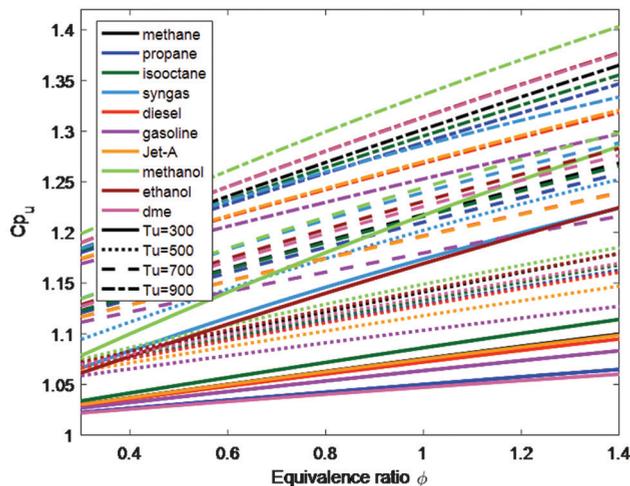


Figure 4. Specific Heat of Unburned Fuel-Air Mixture for Various Fuels at Different Equivalence Ratios and for Different Unburned Mixture Temperatures

difference in adiabatic flame temperature especially for ethanol and methanol in their gaseous and liquid phases as it was already stated that a 90 K increase in flame temperature would double the formation of thermal NO_x . At stoichiometry, differences are 41 K and 70 K respectively. Using gas phase thermodynamic coefficients would cause important deviations in calculation of performance parameters and pollutant emissions such as NO_x and CO which are highly dependent on the flame temperature.

error would cause important deviations in performance estimations and calculation of pollutant emissions such as NO_x and CO which are highly dependent on the flame temperature. As a result, to obtain a correct unburned mixture temperature, adiabatic flame temperature and consequently correct performance results and exhaust gas compositions for liquid fuels, liquid phase polynomial data which can be obtained from the available gas polynomial coefficients should be used.

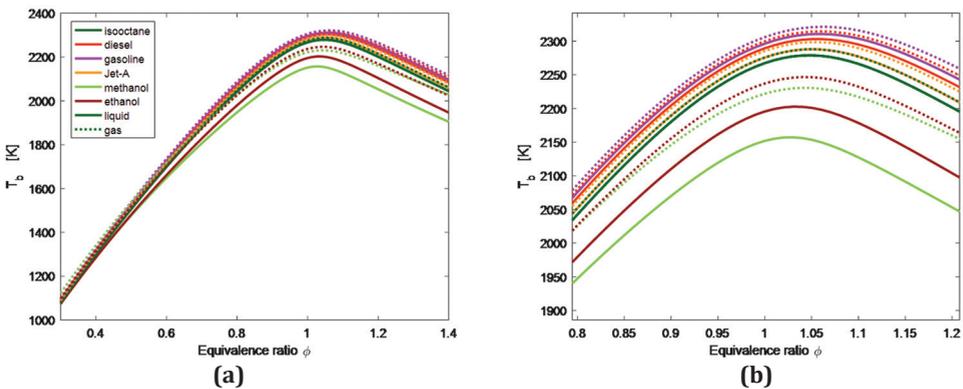


Figure 5. (a) Adiabatic Flame Temperatures of Unburned Fuel-Air Mixture for Various Fuels at Different Equivalence Ratios for Unburned Mixture Temperature of 300 K. **(b)** Zoom in Fig. 5(a)

Conclusions

This paper shows variations of unburned mixture properties with temperature and equivalence ratio for various fuels and states that low temperature ideal gas polynomial coefficients can safely be used for liquid fuels when presented method is applied. Precision of enthalpies and specific heat values of unburned liquid fuels obtained by transformation of the ideal gas polynomial coefficients are satisfactory. For comparison, adiabatic flame temperatures of common liquid fuels are calculated both with available gas phase coefficients and obtained coefficients for liquid phase. According to the results, substantial differences are observed in adiabatic flame temperature especially for ethanol and methanol. Obviously, this

References

- [1] Talay, A. A., Deniz, C. and Durmuşoğlu, Y. (2014). "Gemilerde Verimi Arttırmak İçin Uygulanan Yöntemlerin CO₂ Emisyonlarını Azaltmaya Yönelik Etkilerinin Analizi." *Journal of ETA Maritime Science* 2(1): 61-74.
- [2] Doğan, H. E., Arslan, H. and Mehdiyev, R. (2013). "LPG Dönüşümü Yapılmış Bir Dizel Motorunda Azotoksit Oluşumunun Teorik ve Deneysel Olarak İncelenmesi." *Journal of ETA Maritime Science* 1(2): 27-38.
- [3] Öztürk, E. (2013). "Operational Measures For Energy Efficiency In Shipping." *Journal of ETA Maritime Science* 1(2): 65-72.
- [4] Parlak, A. and Kökkülünk, G. (2016). "BirGemiDizelMotorununPerformans

- Ölçümü ve Değerlendirilmesi." *Journal of ETA Maritime Science* 4(3): 165-173.
- [5] Ferguson, C. R. (2016). *Internal combustion engines : applied thermosciences*. New York, John Wiley.
- [6] Gordon, S. and McBride, B. J. (1971). *Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouguet detonations*. Washington,, National Aeronautics and Space Administration.
- [7] Gardiner, W. C. (1984). *Combustion Chemistry*. New York, Springer-Verlag.
- [8] Heywood, J. B. (1988). *Internal combustion engine fundamentals*. New York, US, McGraw-Hill.
- [9] Rashidi, M. (1998). "Calculation of equilibrium composition in combustion products." *Applied Thermal Engineering* 18(3-4): 103-109.
- [10] Visser, W. P. J. and Kluiters, S. C. A. (1998). *Modelling the effects of operating conditions and alternative fuels on gas turbine performance and emissions*. Netherlands, NLR National Aerospace Laboratory.
- [11] Rakopoulos, C. D., Hountalas, D. T., Tzanos, E. I. and Taklis, G. N. (1994). "A Fast Algorithm for Calculating the Composition of Diesel Combustion Products Using 11 Species Chemical-Equilibrium Scheme." *Advances in Engineering Software* 19(2): 109-119.
- [12] Gonca, G. (2015). "Investigation of the influences of steam injection on the equilibrium combustion products and thermodynamic properties of bio fuels (biodiesels and alcohols)." *Fuel* 144: 244-258.
- [13] Kayadelen, H. K. and Üst, Y. (2017). "Thermodynamic, environmental and economic performance optimization of simple, regenerative, STIG and RSTIG gas turbine cycles." *Energy* 121: 751-771.
- [14] Kayadelen, H. K. and Üst, Y. (2014). *Thermodynamic properties of engine exhaust gas for different kind of fuels*. MFMHMT 2014 - The 2014 International Conference on Mechanics, Fluid Mechanics, Heat and Mass Transfer, Interlaken, Switzerland.
- [15] Kayadelen, H. K. and Üst, Y. (2014). "Performance and environment as objectives in multi-criterion optimization of steam injected gas turbine cycles." *Applied Thermal Engineering* (71): 184-196.
- [16] Kayadelen, H. K. and Üst, Y. (2013). "Prediction of equilibrium products and thermodynamic properties in H2O injected combustion for CHON type fuels." *Fuel* 113: 389-401.
- [17] Kayadelen, H. K. and Üst, Y. (2014). *Thermodynamic properties of engine exhaust gas for different kind of fuels*. *Computational Problems in Science and Engineering*. N. Mastorakis and V. Mladenov. Interlaken, Switzerland, Springer: 247-260.
- [18] *Reaction Design* (2009). *CHEMKIN Pro Release 15083*. San Diego, CA, Reaction Design.
- [19] Morley, C. (2005). "GASEQ, A Chemical Equilibrium Program for Windows Ver. 0.79."
- [20] Habib, M. A., Elshafei, M. and Dajani, M. (2008). "Influence of combustion parameters on NOx production in an industrial boiler." *Computers & Fluids* (37): 12-23.
- [21] Kayadelen, H. K. (2017). *Thermodynamic properties of unburned CHON type fuels, fuel mixtures and reactant mixtures*. *International Conference on Energy and Thermal Engineering, ICTE 2017*, İstanbul, Yildiz Technical University.
- [22] Kuihua, H. and Chunmei, L. (2007).

- "Kinetic Model and Simulation of Promoted Selective Non-catalytic Reduction by Sodium Carbonate." *Chin. J. Chem. Eng.* 15(4): 512-519.
- [23] Lemmon, E. W., Huber, M. L. and McLinden, M. O. (2013). NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1., Gaithersburg, National Institute of Standards and Technology, Standard Reference Data Program.
- [24] Goodwin, R. D. (1989). "Toluene Thermophysical Properties from 178 K to 800 K at pressures to 1000 Bar." *J. Phys. Chem Ref. Data* 18(4): 1565-1636.
- [25] Poling, B. E. and Thomson, G. H. (2008). *Perry's Chemical Engineers Handbook 8th Edition*. U.S., McGraw Hill.
- [26] Lemmon, E. W., Huber, M. L. and McLinden, M. O. (2013). NIST Reference Fluid Thermodynamic and Transport Properties-REFPROP Version 9.1 User's Guide. Gaithersburg, Maryland, National Institute of Standards and Technology, Standard Reference Data Program.
- [27] Olikara, C. and Borman, G. L. (1975). A computer program for calculating properties of equilibrium combustion products with some applications to I.C. engines. Warrendale, Pa., Society of Automotive Engineers.
- [28] Lieuwen, T. C., Yang, V. and R. Yetter, Eds. (2010). *Synthesis Gas Combustion - Fundamentals and Application*. Boca Raton, FL, CRC Press.
- [29] Dooley, S., Wona, S. H., Heyne, J., Farouk, T. I., Ju, Y., Dryer, F. L., Kumar, K., Hui, X., Sun, C.-J., Wang, H., Oehlschlaeger, M. A., Iyer, V., Iyer, S., Litzinger, T. A., Santoro, R. J., Malewicki, T. and Brezinsky, K. (2012). "The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena." *Combustion and Flame* 159: 1444-1466.
- [30] Pitz, W. J. (2009). *Recent Progress in the Development of Diesel Surrogate Fuels*. Georgia, U.S., Coordinating Research Council, CRC Inc.
- [31] Gauthier, B. M., Davidson, D. F. and Hanson, R. K. (2004). "Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures." *Combustion and Flame* 139: 300-311.