Research paper

HTPB-based Binder Surrogates and their Effects on Preliminary Rocket Motor Analyses

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Abstract: This paper presents a comparison of the hydroxyl-terminated polybutadiene (HTPB) models used during conceptual and preliminary rocket propulsion analyses. The HTPB molecular formulas and enthalpies of formation from various literature sources, obtained by different methods, are discussed. It is shown that the range of heats of formation and properties of HTPB-based binders presented in these references are very wide. The Benson additivity rule was used to estimate the HTPB enthalpy of formation and to compare it with values found in the literature. The HTPB binder models are set side by side in terms of solid rocket motor performance and observable combustion products, using chemical equilibrium software. Moreover, simple heat transfer and aluminum combustion models are used to present the impact of using different models of binders on design calculations. It is shown that ammonium perchlorate/ HTPB propellant thermochemical output data may not be valuable, if used without caution. Taking appropriate contingencies into account and understanding what type of model is being used is necessary. The objective of this paper is to turn the attention of the propellant and explosives community to a class of problems that are often overlooked during initial design phases due to propellant composition simplification.

Keywords: hydroxyl-terminated polybutadiene, solid propellant, solid rocket motor, binder

Nomenclature

AP   Ammonium perchlorate
c_i Molar concentration of compound i
d Aluminum agglomerate diameter [µm]
HTPB   Hydroxyl-terminated polybutadiene
p Pressure in combustion chamber [atm]
SRM   Solid rocket motor
T_0 Temperature of primary combustion products [K]
t_b Burn duration of aluminum agglomerate [ms]
X_{eff} Effective oxidization factor

1   Introduction

The most commonly-used heterogeneous solid rocket propellants are based on ammonium perchlorate (AP) as the oxidizer and a binder system with aluminum powder as the main fuel. Typical applications include missiles [1], launch vehicles [2, 3] and sounding rockets [4]. In most propellants several additives are included, such as burn rate modifiers, plasticizers, stabilizers, bonding and processing agents and high energy compounds [5]. The binder system consists of the binder itself and its curative. While various binder systems are utilized [6], hydroxyl-terminated polybutadiene(HTPB) remains the baseline for most applications due to its performance, good mechanical and thermochemical properties and international industrial experience with HTPB-based propellants. Apart from serving as the binder in solid propellants [7, 8], it is also utilized as a fuel in hybrid rocket motors [9, 10]. The vast majority of published research is based on HTPB systems. New HTPB-based propellant formulations are under continual development and the initial research phases include preliminary calculations, considering performance, often accompanied by quantum mechanical calculations on the chemical engineering side [11]. In recent years a better understanding of combustion mechanisms has been achieved and advances in the field of solid rocket motor (SRM) combustion modelling are being made [12, 13]. However, advanced Computational Fluid Dynamics analyses are conducted mostly for large SRMs and their aim is to study specific flow phenomena, rather than only to predict system performance. Advanced ignition and combustion models are available [14, 15]. The baseline

specific impulse prediction methodology has not changed for a number of decades. At the design stage, specific impulse calculations are conducted using chemical equilibrium and chemical kinetics codes and the ratio of the real and calculated performance is computed using semi-empirical correlations [16, 17]. With well over 50 years of experience with HTPB propellants [18], the understanding of particular factors affecting the specific impulse efficiency is high. However, a number of worldwide manufacturers exist and the different industrial processes and technologies used lead to different formulations and therefore different HTPB properties. It can be seen that different research groups use different binder models, not necessarily representing the properties of the HTPB systems available in their country. Also a wide range of heats of formation of HTPB binder systems can be found in the literature. This is due to different degrees of polymerization and curative treatments [19]. Three different polymerization methods allow HTPB to be produced and their impact on the binder properties are discussed in [20]. The present paper has the aim of investigating the impact of using various single-formula HTPB-systems as surrogates on example design considerations.

2   HTPB System Surrogates

HTPB is a long-chain, cross-linked and high molecular-mass polymer [15]. Its referenced polymerization degree starts at 30 [21] and molecular masses up to 9100 g/mol can be found in the literature [22], with 2000-3000 g/mol mentioned most commonly [23]. Data for the popular commercial HTPB types, including R-45HTLO, R-45M and R-20LM, can be found in [24]. Various studies of HTPB properties include research on cross-linking, an increase of which reduces the binder strain capability [25], research considering the NCO-to-OH group ratio (often referred to as R) and the triol-to-diol ratio, all of which have impacts on the overall binder properties [26]. HTPB's main advantages are low glass transition temperature and good combustion performance. Different binder systems are used; curatives and plasticizers differ depending on the propellant's mechanical requirements [27]. Often during conceptual and preliminary studies only the pre-polymer is considered for chemical equilibrium calculations. Table 1 gives an overview of different HTPB formulations and models from recent literature, ordered by the value of their enthalpy of formation. The ones including nitrogen atoms show the impact of the curative, and in some cases plasticizer, used. The average composition, including the effect of the curative, is $C_{7.000}H_{10.734}O_{0.243}N_{0.087}$. Only data for HTPB binder systems without any burn

rate modifiers were selected, since catalysts and burn rate suppressants can be separately included due to their specific formulas, well characterized properties and relatively low contribution in the overall propellant mass. The heats of formation of the listed HTPB models are provided in kJ/kg units instead of kJ/mol, due to better representation of the physical properties at a macro-level (while different molar masses are quoted). The heat (enthalpy) of formation of a given compound is defined as the energy needed to form the compound from its constituent elements, being in their standard states [28]. The standard enthalpy of formation given in the literature presumably corresponds to a pressure of 10^5 Pa and a temperature of 298.15 K. Some additional models were excluded from the present study since they were either incomplete or nearly identical to the ones already listed. While in most cases enthalpies of formation were given explicitly, for the models O and Q they were calculated by this author using the given heat of combustion, basing on the methodology provided in [29]. The formation of H_2O and CO_2 as the main combustion products was assumed. The conducted literature survey showed HTPB-based binder densities varied between 910 and 960 kg/m^3, with an average density of 926 kg/m^3 and a standard deviation of 18.3 kg/m^3. However, the uncured polymer can have a lower density, of the order of 900 kg/m^3 [30]. The higher values within the specified density range are data for binder systems that include plasticizers. While relatively similar chemical formulas are given, the heats of formation found in the literature vary more significantly. The average heat of formation of the models presented in Table 1 is –197 kJ/kg, with a very high standard deviation of 719 kJ/kg.

Table 1. Models of HTPB-based binder systems

| Model	Reference	Chemical elements				Density [kg/m³]	Heat of formation [kJ/kg]
		H	C	O	N		
B	[31]	10.710	7.290	0.100	0.000	–	1002.5
C	[31]	10.580	7.290	0.110	0.000	–	821.2
D	[31]	10.520	7.290	0.120	0.000	–	526.6
E	[32]	988.000	654.000	20.000	8.000	919	514.6
F	[19]	5.808	3.846	0.039	0.000	930	456.5
G	[32]	103.000	73.000	1.000	0.000	919	54.4
I	[33]	10.982	7.337	0.058	0.000	–	−124.1
J	[34]	110.000	73.000	6.000	0.000	–	−125.5
K	[35]	10.650	7.075	0.223	0.063	–	−310.0
L	[36]	302.000	240.000	2.000	0.000	–	−310.0
M	[37]	10.813	7.110	0.138	0.107	960	−315.5
N	[38]	15.400	10.000	0.070	0.000	920	−379.4
O	[7]	11.113	7.110	0.150	0.071	920	−461.8
P	[35]	10.650	7.075	0.223	0.063	–	−579.1
Q	[7]	10.319	6.794	0.444	0.064	940	−582.4
R	[39]	15.400	10.000	0.070	0.000	920	−769.3
S	[40]	109.479	66.881	3.767	1.864	960	−873.2
T	[32]	978.000	656.000	13.000	5.000	911	−2083.6

Two additional formulas can be found in the literature [15, 41]. They do not represent HTPB-based binders but may be useful for simple HTPB decomposition modelling [15] mentions that the main decomposition product is gaseous C_2H_4, accompanied by light hydrocarbon species. Since HTPB decomposition is endothermic, the heat of formation of true HTPB must be lower than in the case of gaseous ethylene. In the case of the second formula, proposed in [41], the actual HTPB prepolymer density is used [30] with the formula approximated as C_4H_6.

Table 2. Formulas useful for HTPB decomposition modelling

Model	Reference	Chemical elements				Density [kg/m³]	Heat of formation [kJ/kg]
		H	C	O	N		
C_2H_4	[15]	4	2	0	0	–	1871.5
C_4H_6	[41]	6	4	0	0	900	0.0

In Table 1, where the HTPB models are collected, both positive and negative values are present, and even the nitrogen-free formulas have a range of heats of formation of approximately 1000 to –800 kJ/kg, which is very wide.

The first three models in Table 1 are taken from one reference [31] and the heats of formation are estimated there using the same calculation approach, making them questionable regarding accuracy. Due to the wide range of heats of formation in Table 1, in the present study care was taken to compare the values with the analytical methods, in order to explain the differences in values. A wide range of existing methods are based on summation of group properties. A good review is presented by Carey and Sundberg in [42]. Modern approaches use Molecular Orbital and Density Functional Theory to obtain the heats of formation. Quantumchemical calculations done to obtain the properties of HTPB were performed by Khan *et al.* [39]. In the present paper a simple, yet not commonly used for HTPB binders, approach is proposed. It is based on the additivity concept of Benson *et al.* [43, 44]. This method is used here due to its good characterization concerning experimental verification and ease of application. For reference, the popular formula of the R-45 polymer is taken from [38]: (OH–(CH₂–CH=CH–CH₂)ₙ–OH. The final binder formula shown in Figure 1 is also used [38].
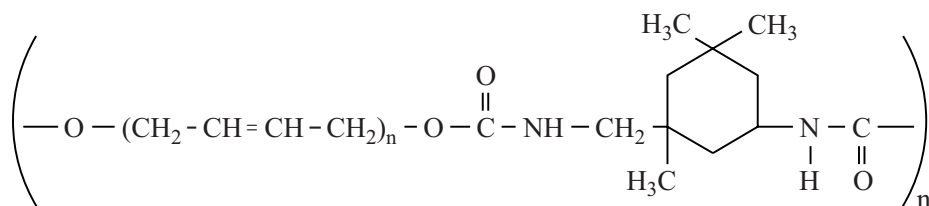

Figure 1.   HTPB binder formula from [38]

The enthalpy of formation of HTPB is estimated here using the Benson method with additivity coefficients taken from [45-47]. Additional coefficients and corrections, including ones due to strain energy, are not considered. Liquid phase heats of formation are analyzed due to the lack of many group additivity values for the solid phase. For groups which contribute to the vast majority of bonds, differences between available values for solid and liquid phases are known and were considered acceptable in order to perform an initial assessment:

(i) $C-(H)_2(C)(C_d)$ (–25.73 kJ/mol for liquid phase and –24.35 kJ/mol for solid phase),

(ii) $C_d-(H)(C)(C_d)$ (31.05 kJ/mol for liquid phase and 25.48 kJ/mol for solid phase).

The results obtained for the R-45 polymer and the cured binder are shown in Figure 2. The value of *n* represents the degree of polymerization, and thus the number of monomer units in the polymer, in this case butadiene.
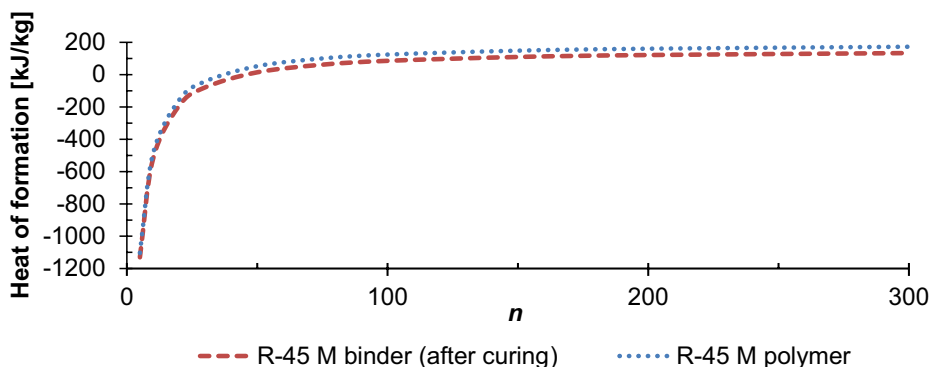
Figure 2. Estimation of binder heat of formation as a function of the degree of polymerization, obtained using the Benson additivity method

The results obtained show that for polymerization degrees of 25 and higher, the expected heat of formation should be between –150 and 200 kJ/kg. A few of the models, mentioned in [32-34], fit within this range [32-34]. Naturally, the use of different curing techniques (it is clear that nitrogen-free formulas have a narrower range of enthalpies of formation) and including plasticizers in the single-formula binder models lead to a wide range of enthalpies of formation [48].

Using a non-computational approach, all binder models are expected to fit into the enthalpy of formation envelope defined by butane and 1,3-butadiene (C_4 aliphatic hydrocarbons are considered with data taken from [49]). Butane is equivalent to the lower limit of enthalpy of formation due to no C=C bonds: –2164 kJ/kg. The upper limit of the binder enthalpy of formation is expected to be defined by 1,3-butadiene due to its very high content of double C=C bonds: 2011 kJ/kg. Indeed, all models investigated fall within the range outlined. A very rough estimate of the enthalpy of formation could be done by reference to 1-butene (11 kJ/kg), since in this case only one of the three bonds between carbon atoms is a double bond, close to what is present in the R-45M binder. For comparison, AP, the most common solid rocket propellant oxidizer has a heat of formation of –2520 kJ/kg [35]. Energetic binders, such as 3,3-bis(azidomethyl)oxetane (BAMO) [50], have high heats of formation, significantly exceeding the most optimistic HTPB model presented within this paper. In the case of BAMO a value of 2460 kJ/kg is provided in [35].

3   Impact of using Different HTPB-based Binder Models

3.1 General information

This paragraph gives a comparison of the basic engineering calculation outputs for each of the HTPB models presented. Straight forward approaches and the simplest methodologies available were used, since a comparison of the various HTPB models is the main aim, instead of detailed SRM modelling. Chemical equilibrium calculations, using NASA Chemical Equilibrium with Applications software [51, 52], have been performed, due to the use of this type of methodology during numerous preliminary analyses conducted worldwide regarding both solid [53, 54] and hybrid rocket propulsion [55, 56]. All of the analyses for solid propellants were done assuming AP/HTPB compositions. The chamber pressure was set to 70 bar and a nozzle pressure ratio of 70 was used, while assuming ideal expansion in the nozzle. The reference temperatures were set to 298.15 K.

## 3.2 Performance of AP/HTPB propellants

The evaluated specific impulses for propellants with different binder contents are presented in Figure 3. While most solid propellants have binder fractions between 12% and 16%, results for contents up to 20% are provided due to 20-to-80 binder-oxidizer ratios being used in several reference propellants [7, 35]. It can be seen that similar optimal oxidizer/fuel ratios are valid for different models, nearly all falling in the range between 10% and 11%. Of course slurry processability limits and mechanical properties considerations give further binder content requirements, leading to practical binder mass contents exceeding 12%.

The propellant using gaseous ethylene instead of HTPB, gives the highest theoretical performance due to over-prediction of the propellant combustion temperature [15]. This model was, however, originally considered for combustion mechanism studies. Polybutadiene-based propellants including plasticizers show lower combustion heat release, due to their high oxygen content [37]. This is observed *via* a decrease in the calculated expected specific impulse, while using the models presented. While relative performance differences between models B-to-T are below 2.6% for the 12% binder content, they are as low as 1.6% if propellant T is excluded from the list (having a drastically lower heat of formation then expected). The range of specific impulses obtained for a given binder content increases when lower solids loadings are considered. As stated, these calculations were performed by assuming optimal flow and expansion conditions. Practical performance is often estimated during conceptual studies as 92% of this value [5].
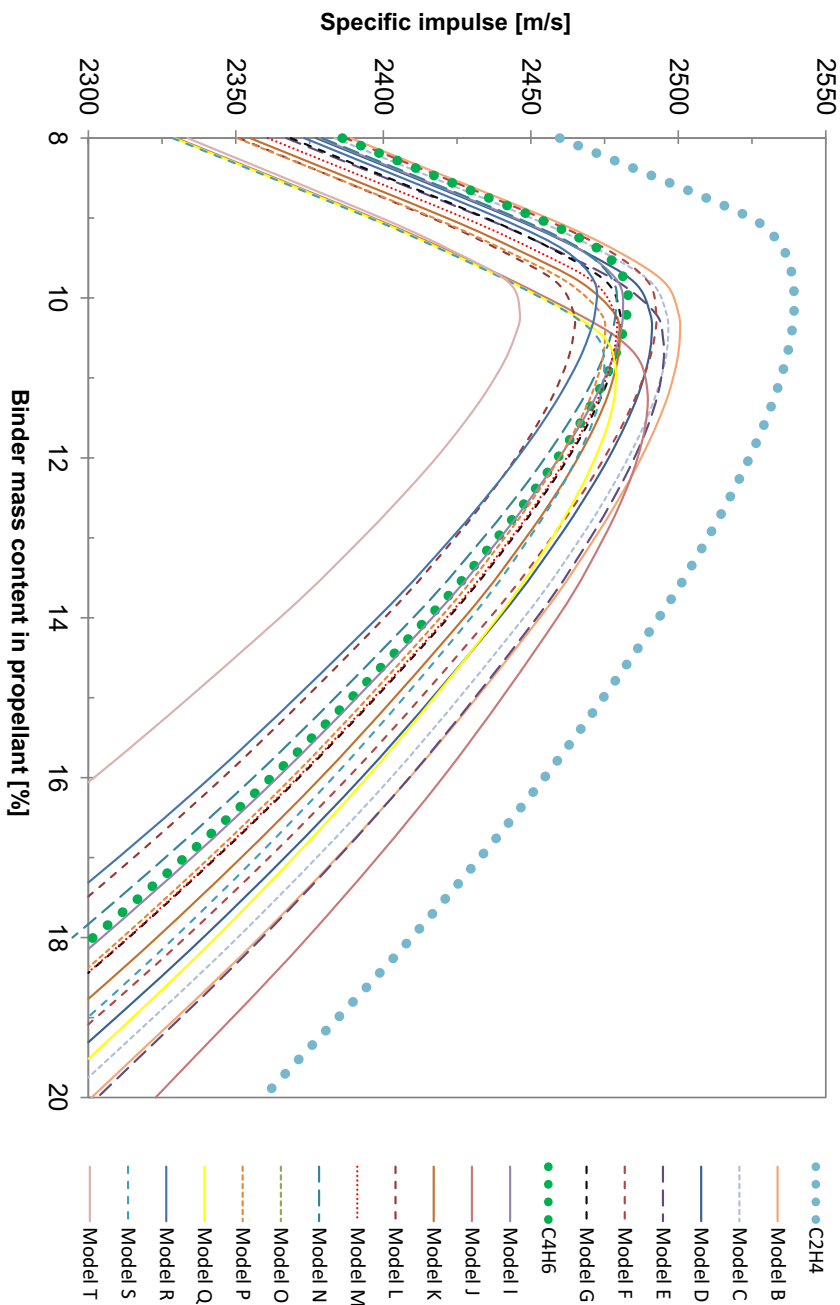
Figure 3. Chemical equilibrium theoretical specific impulses for different unmetallized AP-based solid rocket propellants at 70 bar chamber pressure and 70:1 nozzle pressure ratio
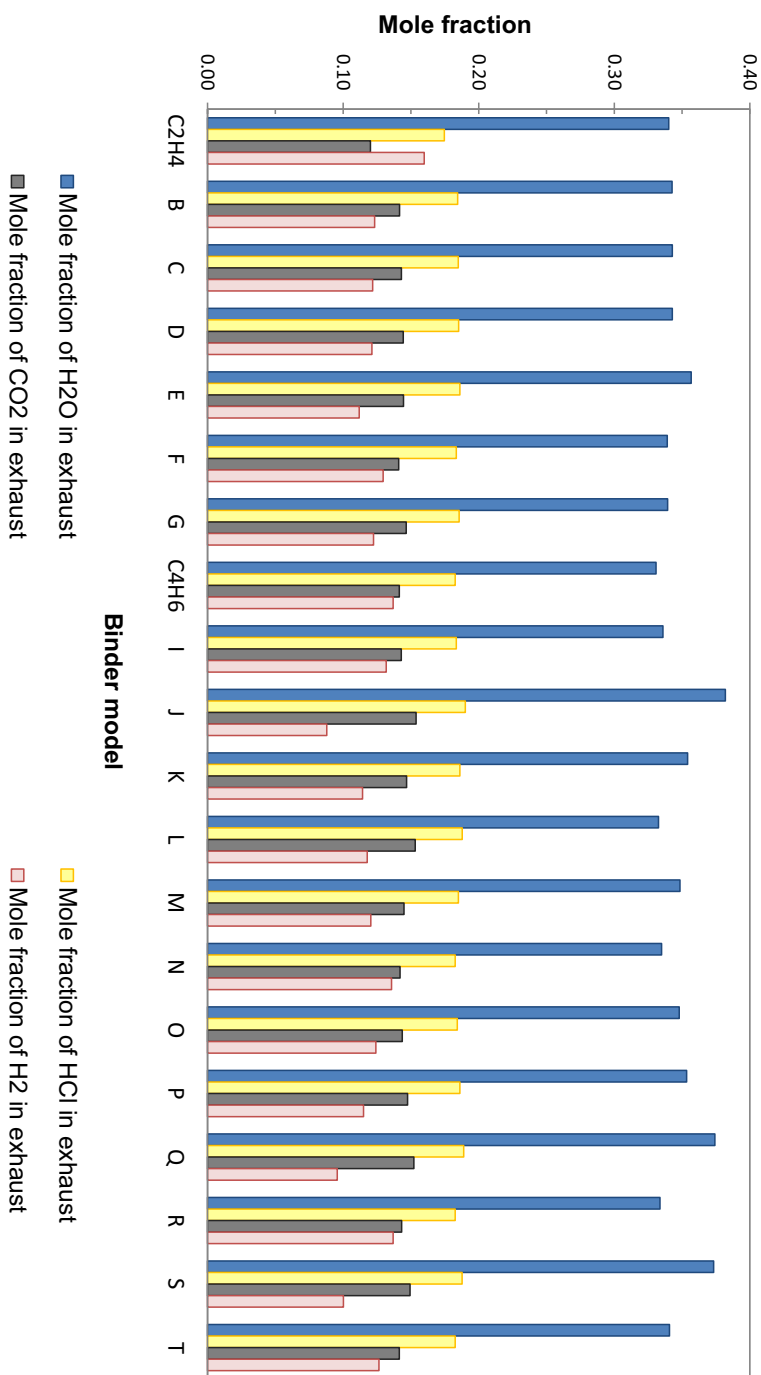
Figure 4. Mole fractions of H_2O, HCl, CO_2 and H_2 combustion products at the nozzle exit, assuming chemical equilibrium

3.3 Exhaust visibility

Exhaust visibility is significant for military missiles with low signature requirements. For non-aluminized reduced-smoke propellants based on AP/HTPB, atmospheric humidity and temperature are key factors affecting missile exhaust visibility [7, 57]. Under adequate conditions, HCl and H_2O form a white fog surrounding the exit plume. Figure 4 presents the mole fractions of key compounds at the nozzle exit for a propellant consisting of 14% binder and 86% of AP. CO_2 and H_2O concentrations are also given due to their significance in the infrared emission of the exhaust. Finally, the presence of H_2 is crucial in terms of afterburning, since it is oxidized and generates additional H_2O in the secondary flame. No additives for afterburning suppression were considered.

It can be seen that for all models the relative concentrations of the four key combustion products are similar, with H_2O dominant and HCl, CO_2 and H_2 following. The H_2O mole fractions are in the range from 0.33 to 0.38. For HCl, being also critical regarding SRM visibility, the mole fractions are within 0.175 to 0.190 for all of the 20 models and the compounds listed in Tables 1 and 2. The HCl content is also of increasing interest due to the goal of reducing the environmental impact of rocket vehicles. As for H_2, naturally selecting C_2H_4 over-predicts the hydrogen content due to the high initial hydrogen content in the modelled binder system in comparison to other models. The lowest expected concentration of H_2 in the combustion products occurs for models J, Q and S. These models have low H/O ratios and little hydrogen is left once most of the hydrogen is used to form H_2O. While chemical equilibrium is considered, one must remember that for relatively low expansion ratios and short nozzles, chemical equilibrium calculations provide only a rough estimate due to not considering outflow kinetics and reaction timescales. In the case of solid propellants with solid particle generation (limited in the case of AP/HTPB unmetallized compositions), ideal gaseous outflow and equilibrium cannot be considered.

3.4 Heat transfer

The impact of HTPB-based binder models on convective heat transfer estimations was analyzed using the Bartz method [58]. The same type of propellant as in point 3.2 was assumed. For flows with low particle concentrations, where convective heat transfer is dominant, the Bartz method is considered acceptable for SRM initial design calculations. Several demonstrations of the successful use of the classic version of the Bartz equation for SRM can be found in the literature [59-61]. In this part of the study, a small SRM with a chamber pressure of 70 bar and a nozzle throat diameter of 50 mm was considered. The mass flow differences
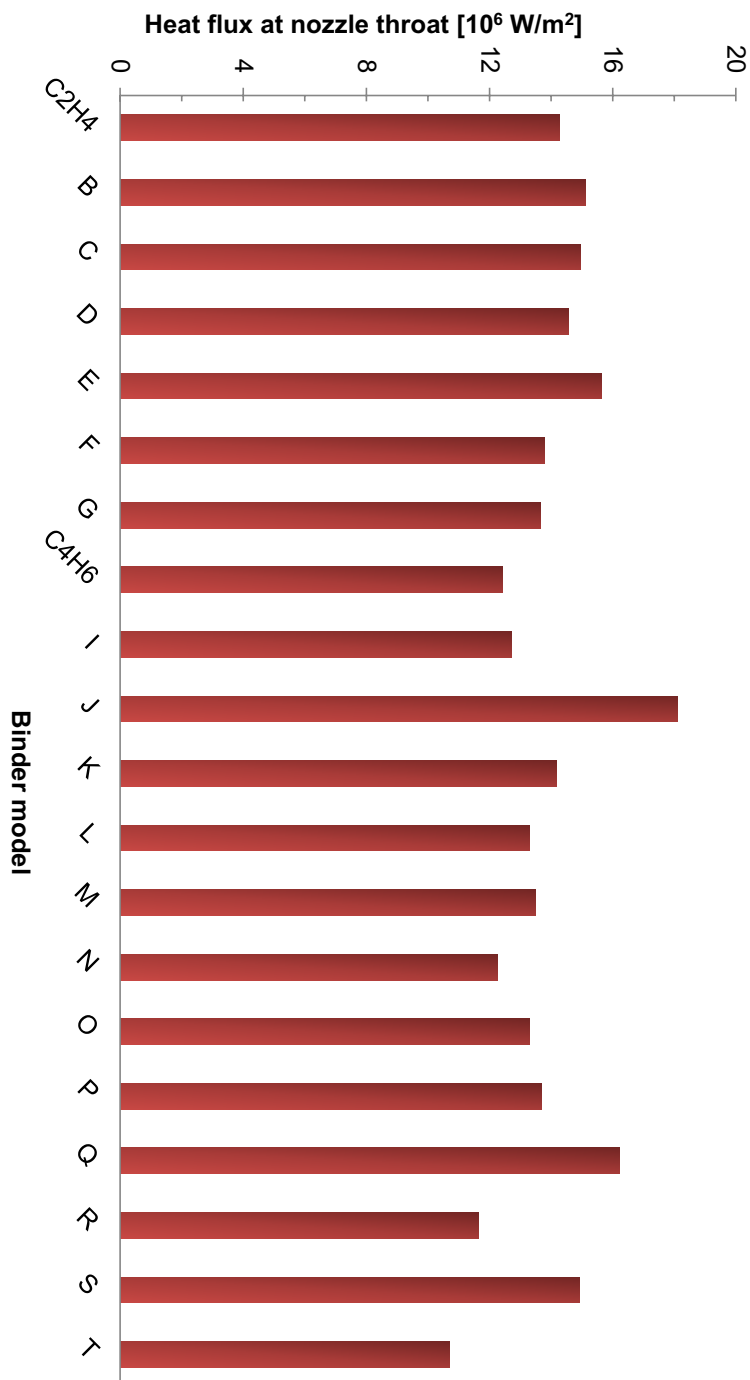
Figure 5. Nozzle throat heat fluxes for propellants using the different binder models

between the models used were minimal (relative standard deviation of below 1%) and therefore the flow rate was set at 8.5 kg/s. Peak heat fluxes in the nozzle, which when using the Bartz equation for classical contours occur exactly at the throat, were obtained. For a given geometry, the flow thermochemical parameters define the convective heat transfer coefficient. Baseline modelling assumptions from [62] and [63] were used. The throat wall temperature was set constant at 2000 K, enabling the influence of the HTPB-based binder models on the computational heat fluxes to be studied. Figure 5 presents the results obtained.

An average convective heat flux of 13.94 MW/m^2, with a standard deviation of 1.55 MW/m^2, was obtained. The difference between the most pessimistic and most optimistic models was over 7 MW/m^2, which may itself be the total heat flux value of a small rocket motor or engine. The variation in the heat flux values was found to be driven mainly by the range of heat capacity ratios of the combustion products for different binder models. However, further analyses should include the total heat flow to a given nozzle geometry. If possible, at this stage, better information on binder properties should be obtained.

3.5 Aluminum combustion modelling

Since most commonly used heterogeneous solid rocket propellants are AP/HTPB compositions with aluminum, a simplified approach to investigate the influence of HTPB models on aluminum combustion predictions was also included in this study. This is especially significant for small SRMs, where particle residence times are low and incomplete combustion may occur. This lead to the development of SRMs using aluminum mass fractions somewhat lower than optimal in terms of the chemical equilibrium calculations. Modelling aluminum particle release, their agglomeration and combustion in SRMs using HTPB is a complex area, with constant research interest [64, 65]. Increased interest also concerns the use of aluminum in hybrid rocket motors. This is due to the potential performance gain, while increased fuel regression rates can be obtained [66, 67]. However, the characteristic velocity and specific impulse can be lower for larger particle diameters, due to incomplete combustion [68]. To use simple models for the purpose of this study, the same propellants as in earlier points were considered with additional aluminum particles present in the flow. For relatively low aluminum mass fractions in solid and hybrid rocket motors, the simplest way of modelling is to exclude aluminum release from the burning surface and analyze its combustion assuming flow properties of a non-aluminized propellant [69]. The fact that AP/HTPB primary combustion takes place in the proximity of the grain surface, and its time scale is over an order of magnitude lower than the time scales of aluminum release, agglomeration and combustion, is used.

The Beckstead model, which considers the influence of different concentrations of key oxidizing species in SRM flows, was applied [70]. The following linear combination of O_2, H_2O and CO_2 concentrations, giving an effective oxidization factor, was implemented:

$$X_{eff} = c_{O_2} + 0.6\, c_{H_2O} + 0.22\, c_{CO_2} \tag{1}$$

The burn duration (in ms) for a spherical agglomerate was calculated as:

$$t_b = \frac{7.35 \cdot 10^{-3} d^{1.8}}{X_{eff}\, p^{0.1}\, T_0^{0,2}} \tag{2}$$

where the diameter was given in µm, the pressure in bar and the temperature in K. Figure 6 presents the results obtained for the combustion of 50 µm aluminum agglomerates. The binder O/C ratio was equivalent to the ratio of oxygen to carbon moles in the various binder-representative compounds. It can be seen that the amount of oxygen within the binder system plays a key role in combustion duration. The burn duration of the considered agglomerate differs by 0.3927 ms when comparing the two extreme HTPB models from Figure 6: J and L. The longer time corresponds to a longer distance travelled by the particle inside the chamber before its combustion. In the case of a flow velocity of 250 m/s within the internal port of the solid propellant grain, the distance differences would be less than 0.1 m, which is negligible for a large SRM, but may be an issue for small auxiliary SRMs.
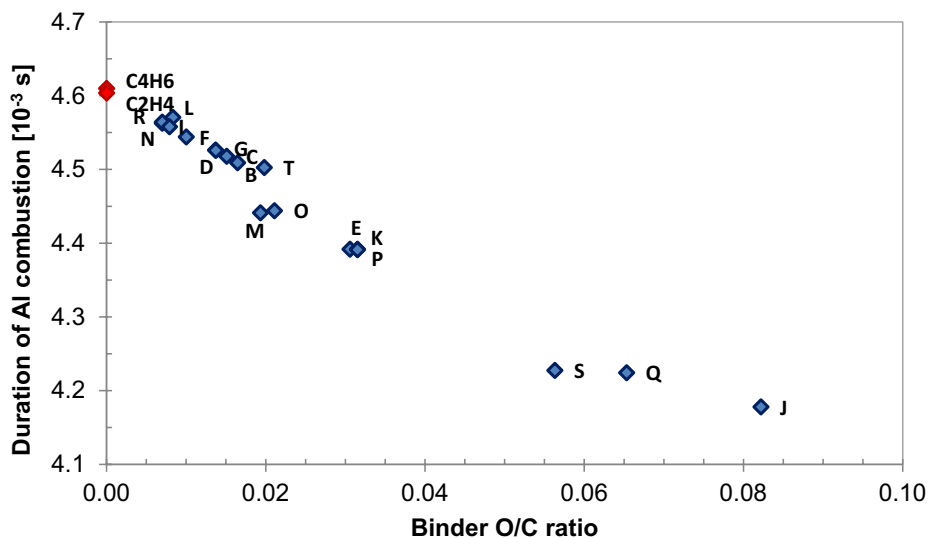
Figure 6. Duration of 50 µm diameter spherical aluminum agglomerate combustion in an example SRM environment as a function of the binder O/C molar ratio

4   Conclusions

♦ Eighteen HTPB-based binder single-formula surrogates from recent literature were presented. Their enthalpies of formation were compared to results obtained using the Benson additivity method, which allows for taking into account the degree of HTPB polymerization. A rule-of-thumb analysis and group additivity estimations gave expected enthalpy of formation levels of ± hundreds of kJ/kg, with values in the higher part of the specified range occurring for higher binder degrees of polymerization. While relatively similar atomic compositions, apart from models being nitrogen-free, are present for the binders reviewed, a very wide range of enthalpies of formation is evident in the literature. Additionally, data and the results of preliminary calculations concerning C_2H_4 and C_4H_6 were compared with the HTPB models. While this gives a total of twenty compositions studied, it is evident that their different chemical formulations and enthalpies of formation affect their performance and combustion properties. The effect of applying different theoretical HTPB models to calculations regarding solid propellants using AP as the oxidizer was studied, in terms

of performance, combustion products, nozzle maximum heat fluxes and aluminum combustion:

(i)   It was shown that relative differences of specific impulse of up to 2.6% between castable AP/HTPB propellants close to their optimal oxidizer-to-fuel mass ratios occur for the assumed SRM operating conditions. However, for non-metalized propellants with 20% binder content, *i.e.* lower performance propellants, the relative difference is up to 7%. It is therefore of utmost importance to take this into consideration while using correction factors for obtaining the expected performance within an SRM. The optimum binder contents in terms of specific impulse are similar: 10-11 wt.%, except for models J, Q, and S, which have different O/C ratios. For propellants that require the addition of a significant amount of plasticizer, appropriate chemical equilibrium inputs should be used. The fact that plasticizers decrease performance was reflected in most of the models studied. This fact should be covered at the earliest possible stages of propulsion system design and accompanied by taking proper margins into account.

(ii)   The thermochemical equilibrium analyses performed for the binder models considered here showed relatively similar combustion product concentrations at the nozzle exit. Regarding plume visibility, HCl and CO_2 concentrations were within a few percent of each other, with slightly larger H_2O concentration variations depending on the model utilized. The exact impact of the differences between models should be assessed by taking into account potential field operations of missiles using particular propellants and a knowledge of the technical parameters of modern plume detection systems, including infrared hardware.

(iii) Major differences can be seen for particular HTPB binder models in the case of nozzle heat flux estimations. The two extreme surrogates gave heat flux levels with a relative difference of 68%. It is not possible to develop a low-mass SRM nozzle assembly if such margins are to be taken into account, regardless of whether ablative nozzle inserts or refractory material nozzle insert technology is used.

(iiii) While the previously summarized analyses considered non-aluminized AP/HTPB propellants, a wide range of rocket motors developed for defense and space applications utilize metalized compositions for increased performance. The calculations conducted here allowed a comparison of the time scales of aluminum particle and aluminum agglomerate combustion in the cases of the binder models discussed. It was shown that model selection is not crucial in the case of aluminum

combustion efficiency modelling, unless SRMs of very small size are considered.

♦ Further discussions on HTPB model utilization shall determine what are the proper margins and design contingencies to be used, depending on the performed calculation and simulation type and the project phase. A critical review of the heats of formation and HTPB formulations found in the literature would require a full database of globally accessible HTPB binders and their sources. With significant data unpublished and technology processes being classified, this remains yet to be done. Specific impulse efficiency cited often in the literature is often difficult to analyze due to the fact that no information on the binder model assumptions are given. Additional caution has to be maintained when using densities for preliminary calculations, as these can vary depending on the HTPB manufacturer and the amount of plasticizer included, which effects the maximum solids loading of the propellant. It is notable that most of the calculations were done for an 86% AP-loaded propellant, while lower oxidizer loadings are also commonly used and in those cases more significant effects of different binder modelling would be seen.

♦ Although this paper focused on SRMs, most of the observations are also applicable to hybrid rocket motors, where the impact of binder modelling is very significant since oxidizer-to-fuel ratios are often lower than for SRMs and HTPB frequently serves as the main fuel.

♦ There is no model that would be on the safe side for all of the aspects considered. It is suggested to be conservative and to use worst-case models for conceptual calculations concerning a given design aspect, unless better knowledge of the binder system to be used is available. It has not been directly assessed whether using a specific binder model is advantageous, but rather differences between existing single-formula surrogates were shown. Studies with experimental data should be carried out for established motor configurations with well-known losses and combustion characteristics.

Acknowledgements

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