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Chapter 18

Thermodynamic Properties of Propanol and Butanol as Oxygenate Additives to Biofuels

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Additional information is available at the end of the chapter

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Abstract

Alternative and renewable energy technologies are being sought throughout the world to reduce pollutant emissions and increase the efficiency of energy use. Oxygenate second-generation biofuels fuels lead to a reduction in pollutant emissions and their thermodynamic and transport properties allow that the facilities for transport, storage and distribution of fuels could be used without modification. Higher alcohols, like propanol and butanol, enhance the octane number, boosting the anti-knock effect in gasoline. Then the compression ratio of the engines can be increased without risk of knocking, leading to higher delivery of power. From the combustion point of view, the production of carbon monoxide and volatile hydrocarbons from the combustion of alcohols is less than the one of gasoline. This chapter covers mixtures of butanol and propanol with hydrocarbons. The properties reviewed are excess volume or density (VE), vapour-liquid equilibrium (VLE), and heat capacity (C_p).

Keywords: butanol, propanol, biofuel, density, enthalpy, phase equilibrium, heat capacity

1. Introduction

Biofuels, as environmental friendly fluids, have been paid much attention over the last decades. They contribute to diminish the greenhouse gas emissions due to its neutral carbon dioxide balance. Moreover, some oxygenated compounds are used as biofuel additives as they lead to

a reduction in pollutant emissions and to an increase in the energy efficiency of vehicle engines [1, 2].

Some alcohols and ethers, as oxygenated compounds additives, are added to present gasoline with the aim of reducing the emission of gases that produce environmental impact. The advantages of these oxygenates can be classified into several categories. First, they can be obtained from renewable, agricultural and raw materials, reducing the dependence of fossil sources [3]. Second, they enhance the octane number, boosting the anti-knock effect in gasoline. Then, the compression ratio of the engines can be increased without risk of knocking, leading to higher delivery of power. From the combustion point of view, the production of carbon monoxide and volatile hydrocarbons from the combustion of alcohols is less than the one of gasoline. Amongst the thermodynamic properties, the heat of vaporization of alcohols is high and leads to a reduction in the peak temperature of combustion, which means lower emissions of nitrogen oxides.

Alternative and renewable energy technologies are being sought to reduce pollutant emissions and increase the efficiency of energy use. Propanol and butanol have been proposed as an alternative to conventional gasoline and diesel fuels [4, 5]. They are higher member of the series of alcohols with each molecule containing three or four carbon atoms rather than two as in ethanol. The EN standards of the European Union (EU) and the World-Wide Fuel Charter (WWFC) for gasoline include, for example, 2-propanol, 2-methyl-2 propanol (also known as tert-butyl alcohol, TBA), and 2-methyl-1 propanol [6, 7] as gasoline components.

The traditional production and consumption of bioethanol have found an alternative with the second-generation biofuels, such as biobutanol. For example, 85% ethanol, E85, needs some modification of the internal combustion engines specifications, unlike butanols, which can work directly in present engines. The energy content per volume unit of butanol is similar to the one of gasoline, and higher than the same for ethanol. Concerning the contribution to the anti-knocking effect, butanol behaves almost the same as other alcohols like methanol or ethanol. And in the presence of water, the mixture butanol/gasoline shows lesser tendency to separation of phases than the mixture ethanol/gasoline. Then, all the facilities for transport, storage and distribution of fuels can be used without modification. Butanol, which can be synthesized chemically or biologically, is an alternative transportation fuel since it has properties that would allow its use in existing engines with minor hardware modifications [5]. For practical purposes, ASTM D7862 [8] gives specifications for blends of butanol with gasoline at 1–12.5% in volume for automotive spark ignition engines. Three butanol isomers are covered by the specification, 1-butanol, 2-butanol, and 2-methyl-1-propanol, while specifically excludes 2-methyl-2-propanol (TBA).

Besides its use as fuel component, its industrial uses covers a broad range of applications as solvent or as reactive for the production of other chemicals. Applications, chemicals and products that use butanol include solvents, plasticizers, coatings, chemical intermediate or raw material, textiles, cleaners, cosmetics, drugs and antibiotics, hormones, and vitamins.

Since the 1950s, most butanol is obtained from fossil sources [6]. 1-butanol and/or 2-butanol could be obtained from reduction of butyraldehyde with hydrogen, which is previously

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obtained by hydroformulation reaction of propene (propyelene). Meanwhile, propylene oxide production leads to isobutene, from which TBA could be derived. Butanol from biomass is called biobutanol [9], and it can be used in unmodified gasoline engines. Biobutanol can be produced by fermentation of biomass by the ABE process [9, 10]. The process uses the bacterium *Clostridium acetobutylicum*, the bacterium for the production of acetone from starch. The butanol was a by-product of this fermentation. Other by-products as acetic, lactic and propionic acids, isopropanol and ethanol, as well as a certain amount of H_2, are generated by the process. *Ralstonia eutropha* can also be used to produce biobutanol, by means of an electro-bioreactor and the input of carbon dioxide and electricity.

According to DuPont [11], existing bioethanol plants can be converted to biobutanol production with low economic cost. The main modification could affect to the fermentation process, with minor changes in distillation, as both alcohols use the same stocks: food energy crops (sugar beets, sugar cane, corn grain, wheat, etc.), non-food energy crops (switchgrass, cellulose, etc.) and agricultural by-products (straw, corn stalks, etc.).

Biopropanol is a rarely discussed biofuel. Tough propanol is included as regular component of gasolines [6], its frequent use as chemical solvent makes it rare to consider it as a fuel. Biopropanol could be produced from microbial fermentation of biomass (cellulose), but the process is extremely inefficient [12]. The issues with microbial production of biopropanol are analogous to the issues with microbial production of biobutanol, so if biobutanol becomes a more practical biofuel to produce, then biopropanol will also become more feasible.

This paper concerns thermodynamic properties of 1-propanol, 2-propanol, 1-butanol, 2-butanol and TBA. Accurate experimental data on thermodynamic properties should be available to check and develop predictive empirical equations, models and simulation programs. Industrial processes as storage, transport, separation and mixing processes also need reliable data for its design. As a result, the experimental literature reviews on properties of pure compounds and its mixtures with characteristic hydrocarbons can provide valuable information about the fluid behaviour under various temperature and pressure conditions.

The paper presents the literature review of available data on thermodynamic properties (density, vapour-liquid equilibrium, specific heat,) of the mixtures of 1-propanol, 1-butanol, TBA and its mixtures with hydrocarbons representatives of gasoline. Density has to do with the volumetric behaviour of the mixtures under pressure and temperature conditions and is the primary data to check equations of state. The vapour-liquid equilibria, which allows the calculation of the Gibbs function, deal with the equilibrium between the liquid and vapour phase under fixed pressure and temperature conditions. And the heat capacity gives information related to the sensible energy storage of the liquids. The review includes only the interval of temperature and pressure of every property reported. The wider is the range of pressure and temperature of the measured properties, so it would be the reliability of the applications of predictive and equations and models. Discussion of further data (uncertainties, experimental apparatus, etc.) would require more space than available. Interested readers should access the literature references to check these issues.

2. The literature review

Thermodynamic properties of liquid propanol and butanol and its liquid mixtures with some hydrocarbon have been obtained from the literature search using online library databases (Web of Science©, Scopus©, NIST© Standard Reference Database) and high impact electronic journals.

Special attention is given to alcohol + hydrocarbon mixtures. As stated, 1-propanol, 1-butanol and TBA have been selected as alcohols. As representative of hydrocarbons, n-heptane, 2,2,4 trimethylpentane (iso-octane), cyclohexane, methyl-cyclohexane, benzene, toluene and 1-hexene have been chosen. They represent linear, branched and cyclic alkanes, aromatics, as well as olefins, which are regular components of gasoline. **Table 1** presents the list of selected compounds.

Compound	CAS number	Chemical formula
Alcohols		
1-Propanol	71-23-8	C_3H_8O
1-Butanol	71-36-3	$C_4H_{10}O$
Tert-butyl alcohol (TBA)	75-65-0	$C_4H_{10}O$
Hydrocarbons		
Heptane	142-82-5	C_7H_{16}
2,2,4 trimethylpentane (TMP)	540-84-1	C_8H_{18}
Cyclohexane	110-82-7	C_6H_{12}
Methyl cyclohexane	108-87-2	C_7H_{14}
Benzene	71-43-2	C_6H_6
Toluene	108-88-3	C_7H_8
1-Hexene	592-41-6	C_6H_{12}

Table 1. Selected alcohols and hydrocarbons.

Concerning properties, there is a huge amount of available thermodynamic data for pure compounds. With respect to the mixtures, density data are shown in **Table 2** for binary mixtures alcohol (1) + hydrocarbon (2). **Tables 3** and **4** present the vapour-liquid equilibria selected for mixtures alcohol (1) + hydrocarbon (2) and alcohol (1) + hydrocarbon (2) + hydrocarbon (3). Finally, heat capacity data for binary mixtures alcohol (1) + hydrocarbon (2) are provided in **Table 5**.

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
1-Propanol	Heptane	[13]	1967	298.15	298.15	101	101
	Heptane	[14]	1967	348.15	348.15	101	101
	Heptane	[15]	1977	298.15	298.15	101	101
	Heptane	[16]	1982	423.11	523.11	422	5495
	Heptane	[17]	1983	298.15	298.15	101	101

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
	Heptane	[18]	1993	313.15	313.15	101	101
	Heptane	[19]	1994	278.15	308.15	101	101
	Heptane	[20]	1995	298.15	298.15	101	101
	Heptane	[21]	1996	298.15	308.15	101	101
	Heptane	[22]	1997	298.15	298.15	101	101
	Heptane	[23]	1998	278.15	308.15	101	101
	Heptane	[24]	2003	308.15	308.15	101	101
	Heptane	[25]	2004	293.15	318.21	101	101
	Heptane	[26]	2005	298.15	298.15	101	101
	Heptane	[27]	2005	298.15	298.15	101	101
	2,2,4 trimethylpentane	[28]	1981	298.15	298.15	101	101
	2,2,4 trimethylpentane	[29]	2007	298.15	298.15	101	101
	2,2,4 trimethylpentane	[30]	2007	303.15	303.15	101	101
	2,2,4 trimethylpentane	[31]	2012	298.15	298.15	101	101
	2,2,4 trimethylpentane	[32]	2015	298.15	323.15	101	101
	Cyclohexane	[33]	1979	298.15	298.15	101	101
	Cyclohexane	[34]	1980	298.15	298.15	101	101
	Cyclohexane	[35]	1991	298.15	298.15	101	101
	Cyclohexane	[36]	1996	298.15	308.15	101	101
	Cyclohexane	[37]	1997	298.15	303.15	101	101
	Cyclohexane	[38]	1998	303.15	303.15	101	101
	Cyclohexane	[24]	2003	308.15	308.15	101	101
	Cyclohexane	[39]	2004	298.15	298.15	101	101
	Cyclohexane	[26]	2005	298.15	298.15	101	101
	Cyclohexane	[40]	2007	293.15	303.15	101	101
	Cyclohexane	[41]	2008	303.15	303.15	101	101
	Cyclohexane	[42]	2016	303.15	313.15	101	101
	Methylcyclohexane	[43]	1977	303.15	303.15	101	101
	Methylcyclohexane	[44]	1996	298.15	298.15	101	101
	Methylcyclohexane	[45]	2006	298.15	308.15	101	101
	Benzene	[46]	1969	298.15	298.15	101	101
	Benzene	[33]	1979	298.15	298.15	101	101
	Benzene	[34]	1980	298.15	298.15	101	101
	Benzene	[47]	1993	308.15	308.15	101	101
	Benzene	[58]	1994	298.15	298.15	101	101
	Benzene	[59]	2001	303.15	303.15	101	101
	Benzene	[24]	2003	308.15	308.15	101	101
	Benzene	[39]	2004	298.15	298.15	101	101
	Benzene	[50]	2007	288.15	313.15	101	101
	Benzene	[51]	2008	298.15	298.15	101	101
	Benzene	[52]	2009	298.15	298.15	101	101

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
	Benzene	[53]	2015	303.15	303.15	101	101
	Toluene	[54]	1980	298.15	298.15	101	101
	Toluene	[47]	1993	308.15	308.15	101	101
	Toluene	[48]	1994	298.15	298.15	101	101
	Toluene	[55]	2000	303.15	313.15	101	101
	Toluene	[24]	2003	308.15	308.15	101	101
	Toluene	[56]	2005	303.15	333.15	100	30000
	Toluene	[57]	2006	298.15	298.15	101	101
	Toluene	[58]	2006	303.15	333.15	101	101
	Toluene	[59]	2008	298.15	298.15	101	101
	Toluene	[53]	2015	303.15	303.15	101	101
	1-Hexene	[60]	1993	298.15	298.15	101	101
	1-Hexene	[61]	2010	298.15	298.15	101	101
1-Butanol	n-Heptane	[15]	1977	298.15	298.15	101	101
	n-Heptane	[62]	1979	298.15	298.15	101	101
	n-Heptane	[17]	1983	298.15	298.15	101	101
	n-Heptane	[63]	1984	298.15	298.15	101	101
	n-Heptane	[64]	1994	313.15	313.15	101	101
	n-Heptane	[21]	1996	298.15	308.15	101	101
	n-Heptane	[65]	1997	293.15	293.15	101	101
	n-Heptane	[66]	1997	288.15	298.15	101	101
	n-Heptane	[24]	2003	308.15	308.15	101	101
	n-Heptane	[67]	2003	316.85	458.15	4930	4930
	n-Heptane	[26]	2005	298.15	298.15	101	101
	n-Heptane	[68]	2006	288.15	308.15	101	101
	n-Heptane	[69]	2009	288.15	308.15	101	101
	2,2,4 trimethylpentane	[65]	1997	293.15	293.15	101	101
	2,2,4 trimethylpentane	[66]	1997	288.15	298.15	101	101
	2,2,4 trimethylpentane	[31]	2012	298.15	298.15	101	101
	2,2,4 trimethylpentane	[70]	2013	298.15	328.15	101	101
	Cyclohexane	[33]	1979	298.15	298.15	101	101
	Cyclohexane	[34]	1980	298.15	298.15	101	101
	Cyclohexane	[71]	1983	298.15	318.15	101	101
	Cyclohexane	[72]	1995	293.15	313.15	101	101
	Cyclohexane	[38]	1998	303.15	303.15	101	101
	Cyclohexane	[73]	2001	298.15	298.15	101	101
	Cyclohexane	[24]	2003	308.15	308.15	101	101
	Cyclohexane	[74]	2005	298.15	313.15	101	101
	Cyclohexane	[40]	2007	293.15	303.15	101	101
	Cyclohexane	[75]	2010	293.15	293.15	101	101
	Cyclohexane	[76]	2014	293.15	333.15	100	100000

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
	Cyclohexane	[42]	2016	303.15	313.15	101	101
	Methylcyclohexane	[43]	1977	303.15	303.15	101	101
	Methylcyclohexane	[77]	1989	298.15	298.15	101	101
	Methylcyclohexane	[78]	2004	303.15	303.15	101	101
	Methylcyclohexane	[45]	2006	298.15	308.15	101	101
	Benzene	[46]	1969	298.15	298.15	101	101
	Benzene	[33]	1979	298.15	298.15	101	101
	Benzene	[34]	1980	298.15	298.15	101	101
	Benzene	[79]	1993	298.15	298.15	101	101
	Benzene	[80]	1994	298.15	308.15	101	101
	Benzene	[81]	1996	308.15	308.15	101	101
	Benzene	[49]	2001	303.15	303.15	101	101
	Benzene	[21]	2003	308.15	308.15	101	101
	Benzene	[82]	2004	303.15	303.15	101	101
	Benzene	[83]	2008	288.15	313.15	101	101
	Toluene	[84]	1940	298.15	298.15	101	101
	Toluene	[54]	1980	298.15	298.15	101	101
	Toluene	[81]	1996	308.15	308.15	101	101
	Toluene	[55]	2000	303.15	313.15	101	101
	Toluene	[24]	2003	308.15	308.15	101	101
	Toluene	[70]	2013	298.15	328.15	101	101
	Toluene	[85]	2015	298.15	328.15	101	101
	1-Hexene	[86]	2013	273.15	333.15	101	101
TBA	n-Heptane	[62]	1979	299.15	299.15	101	101
	n-Heptane	[64]	1994	313.15	313.15	101	101
	n-Heptane	[87]	2011	303.15	323.15	101	101
	2,2,4 trimethylpentane	[88]	1999	298.15	298.15	101	101
	2,2,4 trimethylpentane	[89]	2001	298.15	298.15	101	101
	2,2,4 trimethylpentane	[90]	2005	298.15	318.15	101	101
	Cyclohexane	[71]	1983	298.15	318.15	101	101
	Cyclohexane	[72]	1995	293.15	313.15	101	101
	Methylcyclohexane	[88]	1999	298.15	298.15	101	101
	Benzene	[79]	1993	298.15	298.15	101	101
	Benzene	[91]	1995	313.15	313.15	101	101
	Benzene	[81]	1996	308.15	308.15	101	101
	Benzene	[82]	2004	303.15	303.15	101	101
	Toluene	[81]	1996	308.15	308.15	101	101
	Toluene	[88]	1999	298.15	298.15	101	101
	Toluene	[55]	2000	303.15	313.15	101	101

Table 2. Reported density ($g \cdot cm^{-3}$) for binary mixtures alcohol (1) + hydrocarbon (2).

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
1-propanol	Heptane	[92]	1966	357.72	371.52	101.32	101.32
	Heptane	[14]	1967	347.97	347.97	39.72	73.63
	Heptane	[13]	1967	303.13	333.12	3.92	39.81
	Heptane	[93]	1980	278.16	303.14	1.67	10.17
	Heptane	[16]	1982	423.15	573.15	200	5066
	Heptane	[94]	1991	313.15	313.15	10.95	16.52
	Heptane	[95]	1992	313.15	313.15	9.638	16.428
	Heptane	[96]	1993	303.15	303.15	5.42	10.24
	Heptane	[97]	1995	379.38	475.45	204.5	1032.8
	Heptane	[98]	1995	316.78	357.58	19.60	101.33
	Heptane	[99]	2000	298.15	298.15	–	–
	Heptane	[100]	2004	303.15	343.15	–	–
	2,2,4, trimethylpentane	[28]	1981	328.36	348.50	15.98	72.75
	2,2,4, trimethylpentane	[101]	1994	357.88	365.46	101.3	101.3
	2,2,4, trimethylpentane	[102]	1994	343.15	343.15	42.04	60.07
	2,2,4, trimethylpentane	[29]	2007	303.15	303.15	4.88	10.45
	2,2,4, trimethylpentane	[103]	2011	318.15	318.15	9.00	21.13
	Cyclohexane	[104]	1977	298.15	298.15	2.79	14.29
	Cyclohexane	[105]	1986	347.66	369.17	101.33	101.33
	Cyclohexane	[98]	1995	347.58	347.58	101.33	101.33
	Cyclohexane	[106]	1996	298.15	308.15	2.63	22.1
	Cyclohexane	[107]	1997	323.15	333.15	27.92	61.17
	Cyclohexane	[99]	2000	313.15	343.15	–	–
	Cyclohexane	[108]	2000	298.15	298.15	101.32	101.32
	Methylcyclohexane	[109]	1969	360.13	366.83	101	101
	Methylcyclohexane	[110]	1989	332.98	332.98	29.12	38.60
	Methylcyclohexane	[111]	1997	358.75	373.60	101.3	101.3
	Benzene	[112]	1947	298.94	363.52	13.33	99.99
	Benzene	[113]	1963	349.12	365.92	101	101
	Benzene	[114]	1964	493.16	558.18	2419.4	4904.2
	Benzene	[104]	1977	298.15	298.15	2.79	13.04
	Benzene	[105]	1986	350.03	361.85	101.33	101.33
	Benzene	[115]	1987	313.15	313.15	7.01	25.98
	Benzene	[107]	1997	323.15	333.15	22.02	56.70
	Benzene	[116]	2001	313.15	313.15	7.047	26.069
	Benzene	[117]	2006	313.15	313.15	7.00	25.91
	Benzene	[52]	2008	323.15	323.15	17.98	39.89
	Benzene	[51]	2008	329.45	368.35	50	94
	Toluene	[115]	1987	313.15	313.15	7.01	11.35
	Toluene	[118]	1996	298.15	298.15	2.63	5.39
	Toluene	[119]	2003	293.15	370.15	–	–

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
	Toluene	[59]	2008	333.15	333.15	20.27	27.41
	Toluene	[120]	2009	323.15	323.15	13.42	17.85
1-butanol	Heptane	[121]	1966	361.92	376.92	91.2	91.2
	Heptane	[122]	1967	387.93	434.34	192.65	496.63
	Heptane	[63]	1984	333.15	363.15	8.01	89.49
	Heptane	[123]	1990	353.15	373.15	101.32	101.32
	Heptane	[124]	1994	313.15	313.15	4.39	13.22
	Heptane	[98]	1995	312.34	357.58	12.93	74.47
	Heptane	[125]	1996	328.45	366.55	25.63	101.38
	Heptane	[126]	1997	303.15	303.15	1.35	8.26
	Heptane	[99]	2000	298.15	298.15	–	–
	Heptane	[127]	2001	365.05	389.05	95	95
	Heptane	[100]	2004	303.15	343.15	–	–
	Heptane	[138]	2010	349.00	387.75	53.3	91.3
	Heptane	[129]	2012	313.15	313.15	2.51	13.22
	2,2,4-trimethylpentane	[130]	2006	308.15	318.15	2	17
	2,2,4-trimethylpentane	[103]	2011	318.15	318.15	7.2	16.4
	2,2,4-trimethylpentane	[129]	2012	313.15	313.15	2.55	13.71
	2,2,4-trimethylpentane	[131]	2013	313.15	313.15	11.55	13.50
	Cyclohexane	[132]	1968	353.15	383.12	21.23	229.21
	Cyclohexane	[133]	1982	293.15	293.15	–	–
	Cyclohexane	[71]	1983	318.15	318.15	3.41	30.59
	Cyclohexane	[134]	1990	312.8	389.9	–	–
	Cyclohexane	[98]	1995	352.7	352.7	101.33	101.33
	Cyclohexane	[108]	2000	298.15	298.15	101.32	101.32
	Cyclohexane	[99]	2000	313.15	343.15	–	–
	Cyclohexane	[135]	2001	350.95	389.05	95	95
	Cyclohexane	[136]	2002	325.6	386.12	40.0	101.3
	Cyclohexane	[129]	2012	313.15	313.15	2.51	24.83
	Methylcyclohexane	[109]	1969	369.75	385.65	101	101
	Methylcyclohexane	[110]	1989	332.98	332.98	11.07	29.77
	Methylcyclohexane	[111]	1997	368.45	390.50	101.3	101.3
	Benzene	[137]	1939	298.15	298.15	0.85	12.59
	Benzene	[128]	1963	353.21	390.83	101.32	101.32
	Benzene	[114]	1964	513.17	558.18	2032.6	4751.2
	Benzene	[115]	1987	313.15	313.15	2.52	24.37
	Benzene	[79]	1993	298.15	298.15	0.82	12.83
	Benzene	[139]	1995	354.03	425.26	105	303
	Benzene	[140]	2004	308.15	308.15	4.03	20.28
	Benzene	[141]	2006	313.15	313.15	2.49	24.37
	Toluene	[84]	1940	376.12	390.83	101	101

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
	Toluene	[142]	1963	378.63	390.83	101.33	101.33
	Toluene	[115]	1987	313.15	313.15	2.52	8.48
	Toluene	[134]	1990	349.5	389.9	–	–
	Toluene	[143]	1997	360.9	389.1	56.4	94.0
	Toluene	[119]	2003	323.15	390.15	–	–
	Toluene	[140]	2004	308.15	308.15	2.49	6.39
	Toluene	[129]	2012	313.15	313.15	2.49	8.39
	1-hexene	[131]	2013	313.15	313.15	2.48	44.99
TBA	Heptane	[145]	1982	313.15	313.15	12.33	19.23
	Heptane	[146]	1983	352.47	371.42	101	101
	Heptane	[124]	1994	313.15	313.15	14.81	19.20
	Heptane	[147]	1995	351.40	368.23	101.3	101.3
	Heptane	[127]	2001	352.25	369.45	95	95
	2,2,4-trimethylpentane	[148]	1999	352.4	372.5	101.3	101.3
	2,2,4-trimethylpentane	[89]	2001	318.13	339.28	15.85	59.49
	2,2,4-trimethylpentane	[149]	2006	353.35	370.55	95.8	95.8
	Cyclohexane	[150]	1976	344.43	354.33	101	101
	Cyclohexane	[71]	1983	318.15	318.15	18.11	36.23
	Cyclohexane	[151]	1985	328.19	343.28	30.43	95.1
	Cyclohexane	[98]	1995	295.35	344.28	13.46	101.40
	Methylcyclohexane	[110]	1989	332.98	332.98	30.44	46.33
	Methylcyclohexane	[148]	1999	353.1	374.0	101.3	101.3
	Benzene	[152]	1902	347.10	347.10	100.66	101.32
	Benzene	[153]	1933	347.10	347.10	–	–
	Benzene	[137]	1939	298.15	298.15	5.60	13.96
	Benzene	[154]	1969	318.15	318.15	18.12	34.32
	Benzene	[155]	1977	346.58	353.98	101	101
	Benzene	[79]	1993	298.15	298.15	5.59	14.83
	Benzene	[98]	1995	296.66	347.19	13.59	101.51
	Benzene	[156]	1998	308.15	308.15	10.18	23.48
	Toluene	[156]	1998	308.15	308.15	6.40	12.97
	Toluene	[148]	1999	355.4	383.8	101.3	101.3

Table 3. Reported vapour-liquid equilibria for binary mixtures alcohol (1) + hydrocarbon (2).

Substance 1	Substance 2	Substance 3	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
1-butanol	2,2,4-trimethylpentane	1-hexene	[131]	2013	313.15	313.15	2.48	44.99
1-butanol	toluene	1-hexene	[144]	2015	313.15	313.15	2.51	44.99
TBA	Cyclohexane	Benzene	[98]	1995	294.91	344.25	13.61	101.36

Table 4. Reported vapour-liquid equilibria for ternary mixtures alcohol (1) + hydrocarbon (2) + hydrocarbon (3).

Substance 1	Substance 2	References	Year	T_{min}/K	T_{max}/K	P_{min}/kPa	P_{max}/kPa
1-propanol	Heptane	[157]	1976	298.15	298.15	101	101
	Heptane	[158]	1981	184.97	300.00	101	101
	Heptane	[159]	1993	298.15	298.15	101	101
1-butanol	Heptane	[159]	1993	298.15	298.15	101	101
	2,2,4 Trimethylpentane	[160]	2012	293.15	313.15	101	25,000
	Cyclohexane	[76]	2014	293.15	313.15	101	25,000
	Toluene	[161]	1991	298.15	368.15	101	101
	1-Hexene	[86]	2013	293.15	313.15	101	25,000

Table 5. Reported heat capacity for binary mixtures alcohol (1) + hydrocarbon (2).

3. Discussion

3.1. Density of mixtures 1-propanol, or 1-butanol, + hydrocarbon

Table 2 presents density data for the selected mixtures alcohol (1) + hydrocarbon (2). Fifty-nine references correspond to mixtures 1-propanol (1) + hydrocarbon (2) and 51 to the one 1-butanol (1) + hydrocarbon (2), while only 16 references have been found for TBA (1) + hydrocarbon (2).

For 1-propanol (1) + hydrocarbon (2), only atmospheric pressure density data have been found for the binary mixtures, except Refs. [16, 56] that are above 5 MPa. The highest pressure, 30 MPa, is reported by Zeberg-Mikkelsen and Andersen [56]. Temperatures above 350 K are only measured by Zawisza and Vejrosta [16]. Concerning 1-butanol (1) + hydrocarbon (2), Refs. [67, 76] report pressure above the atmospheric pressure. Hundred Megapascal is the maximum pressure measured in Ref. [76]. Reference [67] also reports temperature above 350 K. Finally, mixtures TBA (1) + hydrocarbon are reported only at atmospheric pressure and moderate temperatures, being 323.15 K the highest measured temperature [87]. No data were found for the mixture TBA (1) + 1-hexene (2).

3.2. Vapour-liquid equilibrium of mixtures 1-propanol, or 1-butanol, + hydrocarbon

With respect to the binary mixtures, **Table 3** shows 43 references for VLE data on 1-propanol (1) + hydrocarbon (2), 47 for 1-butanol (1) + hydrocarbon (2) and 24 for TBA (1) + hydrocarbon (2). No references for the mixtures 1-propanol (1) + 1-hexene (2) and TBA (1) + 1-hexene (2) were found, while [131] was the only one for 1-butanol (1) + 1-hexene (2). Most references were found for pressures lower or equal to atmospheric pressure. Studies done in Refs. [97, 122, 132] were measured at moderate pressures, below 1.0 MPa, and only Ref. [114] reports pressure close to 5 MPa for both mixtures 1-propanol (1), or 1-butanol (1), + benzene (2).

Concerning temperature, most measurements were performed at low and moderate temperatures. Within the interval 350–400 K, we found a limited number of 27 set of data [51, 63, 84, 98, 105, 109, 111–113, 119, 121, 123, 125, 127, 128, 132, 134–136, 142, 143, 146–150, 155]. Only Refs. [16, 97, 114, 122, 139] report temperatures between 400 and 573 K.

Only three references were found reporting VLE data of ternary mixtures, as shown in **Table 4**, at atmospheric or lower pressures. Temperatures were moderate, with maximum at 344 K measured in Ref. [98]. No ternary mixture with 1-propanol was found.

3.3. Heat capacity of mixtures 1-propanol, or 1-butanol, + hydrocarbon

Only eight references reporting heat capacity of binary mixtures alcohol (1) + hydrocarbon (2) are cited. Three of them correspond to the binary mixture 1-propanol (1) + heptane (2) at atmospheric pressure and at moderate temperatures (up to 300 K). No other mixture of 1-propanol with the any of selected hydrocarbons was found.

While the heat capacity of 1-butanol with heptane, 2,2,4 trimethylpentane, cyclohexane, toluene and 1-hexane was measured by several authors. It must be pointed out that some measurements [86, 160, 161] have been performed at pressures up to 25 MPa and temperature of 313 K.

4. Conclusion

The literature review on thermodynamic properties of liquid mixtures of 1-propanol, 1-butanol and TBA with representative hydrocarbons has been reported. Seven hydrocarbons (linear, branched and cyclic alkanes, aromatics, and olefins) have been selected as representative of present and future unleaded gasoline. The review covers density, vapour-liquid equilibrium and heat capacity of mixtures.

The review of density data shows a big amount of data at low pressure and moderate temperatures. Only two references report data above 30 MPa at a maximum temperature of 333 K. And at temperatures above 450 K, the maximum pressure is 5.5 MPa. With respect to the vapour-liquid equilibrium, only one reference shows measurements over 555 K at 5 MPa. Heat capacity data of mixtures are very scarce, tough some high pressure and high temperature data can be found for some alcohol + hydrocarbon mixtures.

The performance of fuels and biofuels in engines and other devices shows a trend of increasing pressure and temperature, which leads to the need of more reliable predictive models for complex mixtures at such conditions. Availability of high pressure and high temperature thermodynamic properties is then a requisite for the implementation of these equation and models. The review shows a lack of reliable data at high pressure and high temperature thermodynamic data, which serve as a basis for the development of predictive equations and models.

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