

# Lower Flammability Limits of Hydrogen and Light Hydrocarbons at Subatmospheric Pressures

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**ABSTRACT:** The knowledge of flammability limits is essential in the prevention of fire/explosion when handling combustible gases and vapors. In this study, the lower flammability limits (LFLs) of hydrogen–air, methane–air, ethane–air, *n*-butane–air, and ethylene–air were measured in a closed cylindrical vessel (inner diameter 10.22 cm, length 100 cm) with upward flame propagation, at room temperature (20 °C) and initial pressure of 1.0, 0.7, 0.5, 0.3, and 0.1 atm. The LFL of hydrogen initially decreased with pressure from 1.0 to 0.3 atm, and then the LFL increased with the further decrease of pressure. In contrast, the LFLs of the hydrocarbons increased when the pressure decreased from 1.0 to 0.1 atm, except for methane for which the LFL did not change with pressure. The adiabatic flame temperatures (AFTs) at the obtained LFL concentrations of hydrogen and the hydrocarbons were also calculated at subatmospheric pressure conditions. The behaviors of the AFTs of hydrogen and the hydrocarbons were similar to those of the LFLs under the influence of low pressures. On average, at initial pressures from 1.0 to 0.1 atm and LFL concentration, the AFT of hydrogen was 730 K, of the alkanes was 1900 K, and of ethylene was 1800 K. On the basis of the LFLs and AFTs, the risk/hazard associated with fire/explosion of hydrogen and the hydrocarbons at subatmospheric pressures was also discussed.

## 1. INTRODUCTION

A flammable gas or vapor burns in air over a limited range of compositions bounded by two limits of flammability: upper flammability limit (UFL) and lower flammability limit (LFL). UFL is the maximum concentration of gas in air and LFL is the minimum concentration of gas in air capable of propagating flame upon ignition;<sup>1,2</sup> both limits define the range of gas concentration where it is flammable. Both UFL and LFL change with variations in temperature and pressure.

Controlling the concentrations of gases and vapors outside their flammability ranges is a major consideration in occupational safety and health. Flammable gases are stored safely by keeping the gas concentrations above their UFLs. To prevent the existence of a flammable gas–air mixture, a number of methods are employed including the use of inert substances such as nitrogen or carbon dioxide to dilute the gas before it comes in contact with air.<sup>3</sup> For example, nitrogen is commonly used in the procedure to take a vessel containing a flammable gas out of service without creating a flammable environment. The calculation of the amount of nitrogen needed requires the knowledge of the LFL of the gas as illustrated in the following equation:<sup>3</sup>

$$\text{OSFC} = \frac{\text{LFL}}{1 - z\left(\frac{\text{LFL}}{21}\right)}$$

where OSFC is the out of service gas concentration, and *z* is the stoichiometric oxygen coefficient from the combustion reaction between the flammable gas and oxygen. Knowledge of LFL is important in the design of ventilation systems to control flammable gas releases. UFLs and LFLs are also regularly used in consequence modeling and risk assessment of fire and explosion.<sup>4–6</sup> All the above examples show that the knowledge of flammability limits is essential in the prevention of fire and

explosion when handling flammable gases or vapors. Because flammability limits are affected by various factors, it is equally important that the correct flammability limits are selected and used according to the operation conditions, most notably temperature and pressure. As mentioned in our previous study,<sup>7</sup> the increasing presence of hydrogen and hydrocarbons in various laboratory and industrial processes operating at different conditions including subatmospheric pressure conditions (e.g., vacuum drying, vacuum distillation)<sup>8</sup> and the lack of study on their flammability limits at these conditions justify the need to investigate the flammability limits of hydrogen and the hydrocarbons at reduced pressures.

In a previous study,<sup>7</sup> we experimentally determined the UFLs of hydrogen and light hydrocarbons (methane, ethane, *n*-butane, and ethylene) at subatmospheric pressures. It was found that the UFL of hydrogen behaved differently compared to the those of the hydrocarbons under the influence of low pressures; for example, the UFL of hydrogen increased when the pressure decreased from 1.0 to 0.3 atm, while the UFLs of the hydrocarbons decreased with pressure.<sup>7</sup> This unique behavior of the UFL of hydrogen requires special attention when handling hydrogen at low pressure conditions.<sup>7</sup>

As a continuation of the previous study to obtain a complete view of the flammability limits of hydrogen and the hydrocarbons at subatmospheric pressures, we investigated the LFLs of hydrogen, methane, ethane, *n*-butane, and ethylene determined with the same experimental setup, consisting of a closed cylindrical vessel with a bottom ignition source; all

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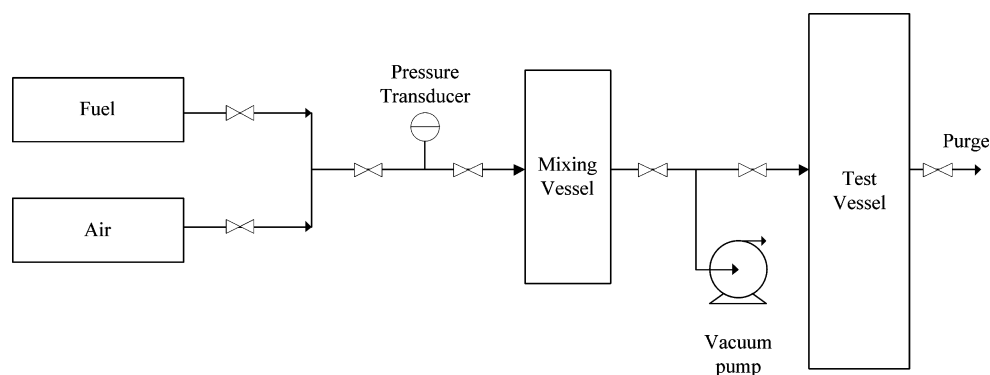


Figure 1. Experimental procedure.

Table 1. Specifications of Fuels and Air Used in the Experiments<sup>a</sup>

	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>2</sub> H <sub>4</sub>	air
purity, %	99.999	99.99	99.995	99.98	99.995 (H <sub>2</sub> O < 1 ppm)	ultra zero certified (H <sub>2</sub> O < 2 ppm)

<sup>a</sup>Data provided by Matheson Tri Gas.

experiments were carried out at room temperature (20 °C) and initial pressures ranging from 1.0 to 0.1 atm. The influence of low pressure on the LFLs of hydrogen and the hydrocarbons was analyzed, and together with the UFLs generated in the previous study, the risk of fire/explosion of the chemicals was discussed.

Besides flammability limits, flame temperature is another important parameter used in the risk assessment of fire/explosion scenarios. For example, flame temperature is used in the consequence analysis of various fire models (e.g., flash fire, jet fire, pool fire, etc.) to calculate the thermal radiation, which is proportional to the fourth power of flame temperature.<sup>6</sup> Adiabatic flame temperature (AFT) is the temperature of flame obtained without heat loss to the surrounding; thus, it is often considered the maximum flame temperature.<sup>9</sup> AFT is widely used to predict various fire/explosion safety parameters such as LFLs of fuel mixtures<sup>10,11</sup> and limiting oxygen concentration<sup>12</sup> with a high level of accuracy. AFT can be calculated based on the law of thermodynamics and chemical equilibrium. There are a number of methods used to calculate AFT of a combustible mixture ranging from simple empirical equations/graphs<sup>13,14</sup> to more complex computer codes.<sup>10,15–17</sup> In this work, the adiabatic flame temperatures of hydrogen and the hydrocarbons at the obtained LFLs of the chemicals were calculated at room temperature and initial pressures ranging from 1.0 to 0.1 atm using CHEMKIN package<sup>17</sup> with thermodynamics properties from the database compiled by Kee et al.<sup>18,19</sup> and reaction mechanism from GRI Mech 3.0<sup>20</sup> and the Combustion Chemistry Center.<sup>21</sup> This computer package has been validated extensively with experimental data<sup>20,21</sup> and used by a great number of researchers to accurately estimate flame temperature and other properties of the combustion process.<sup>22–25</sup>

## 2. EXPERIMENTAL SECTION

The lower flammability limits were determined with upward flame propagation in a stainless steel (SS 316) cylindrical test vessel with a design similar to that used by the US Bureau of Mines<sup>1</sup> and the more recent European standard EN 1839 (T).<sup>26</sup> The vessel was 100 cm long with an inner diameter of 10.12 cm and outer diameter of 11.43 cm. The ignition source was an exploding fuse wire type which was capable of providing

10 J of energy consistently. The pressure inside the test vessel was measured by a pressure transducer placed at the top of the vessel. A set of five thermistors was positioned along the center axis of the test vessel to detect flame propagation. The distance between the top thermistor and the igniter was 75 cm. The experiments were carried out at room temperature (20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, and 0.1 atm.

The experimental procedure is illustrated schematically in Figure 1 and briefly described below. Further details about the apparatus and procedure can be found in previously published works.<sup>7,27</sup>

Ultrahigh purity fuel and air were loaded into a mixing vessel to prepare a test mixture. The specifications of the fuel and air are presented in Table 1. The quantities of the fuel and air were determined based on partial pressure. The uncertainty associated with the LFLs was estimated using the combined standard uncertainty method,<sup>28,29</sup> which was based on random errors associated with the calibration and measurement of the amount of test substance (fuel) in the test mixture and the uncertainty associated with the sampling interval.<sup>7</sup> The maximum uncertainty was estimated at 0.15 mol %. After the mixing, the mixture was allowed to flow into the test vessel where it was ignited from the bottom. The flame propagation was monitored by the thermistors inside the vessel. After the combustion, the vessel was flushed with nitrogen to remove all test products. The whole system was then evacuated to prepare for the next experiment.

A mixture is considered flammable if, upon ignition, it can propagate flame to the top thermistor (75 cm away from the igniter), and is classified as continuous flame propagation.<sup>27,30</sup> Because of the probabilistic nature of flame propagation for mixtures near the flammability limit, a mixture which displays continuous flame propagation in one experiment may not do so in another experiment with the same setup and conditions.<sup>27</sup> Therefore, to determine the flammability limit, 10 repetitive experiments were carried out with the same composition mixture, and the number of continuous flame propagations was recorded. The fuel concentration which had the probability of continuous flame propagation equal or less than 50% compared to the nearest concentration having more than 50% of flame propagation was chosen as the flammability limit.<sup>7,27</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Lower Flammability Limit (LFL) of Hydrogen at Atmospheric Pressure.** The obtained LFL of hydrogen in air at atmospheric pressure is presented in Table 2. For

**Table 2. LFL of Hydrogen in Air at Atmospheric Pressure and Room Temperature**

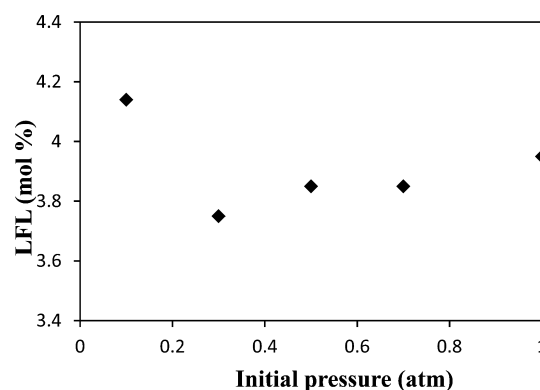
fuel	this work (mol %)	previous work (mol %)	apparatus type	FL criteria
H <sub>2</sub>	3.95 ± 0.15	4.15 <sup>a</sup>	vertical glass tube (ID 7.5 cm, length 150 cm) <sup>1</sup>	visual
		3.90 <sup>a</sup>	vertical stainless steel tube (ID 5.08 cm, length 100 cm) <sup>31</sup>	thermal
		3.75 <sup>a</sup>	glass flask V = 5 dm <sup>3</sup> ASTM E681-01 <sup>26</sup>	visual
		3.80 ± 0.20	vertical glass tube (ID 6 cm, length 30 cm) DIN S1649-1 <sup>26</sup>	visual
		3.60 ± 0.20	glass cylinder (ID 8 cm, length 30 cm) EN 1839 (T) <sup>26</sup>	visual

<sup>a</sup>No information about the uncertainty range.

comparison, the LFLs of hydrogen determined under the same conditions as those used by various research groups but with different experimental setups and criteria are also provided in Table 2. Overall, the obtained LFL is similar to the values generated by apparatuses and criteria consistent with the U.S. Bureau of Mines method.<sup>1,31</sup> The LFLs determined by European methods DIN S1649-1 and EN 1839 (T) are smaller and thus more conservative because European methods use different measurement criteria and flammability limit definition. DIN S1649-1 and EN 1839 (T) require a smaller flame propagation distance (10 cm) for a gas mixture to be considered flammable and define the flammability limit as the concentration where the mixture cannot propagate flame.<sup>7,26</sup>

Together with the upper flammability limit (UFL) generated in our previous study,<sup>7</sup> the flammable region of hydrogen in air at atmospheric pressure and room temperature is 3.95–75.73 mol %, which is much wider compared to that of common hydrocarbons, such as methane (5.35–15.40 mol %) or ethylene (2.85–30.61 mol %).<sup>7</sup> This confirms previous studies about the high hazard and risk of fire/explosion of hydrogen under atmospheric conditions.<sup>4,32</sup>

**3.2. Lower Flammability Limit (LFL) of Hydrogen at Subatmospheric Pressures.** The LFL of hydrogen in air at subatmospheric pressures is summarized in Table 3 and illustrated by Figure 2. Table 3 also includes the UFL of hydrogen determined under the same conditions as those in an



**Figure 2.** Lower flammability limit of hydrogen in air at subatmospheric pressures and room temperature.

earlier study<sup>7</sup> for complete information about the flammability range of hydrogen. For conciseness and clarity, error bars are not included in Figure 2 and other figures in this paper. Initially, the LFL decreased when the pressure was reduced from 1.0 to 0.3 atm, and then the LFL started to increase with a further decrease of pressure. The decrease of the LFL implies an increased risk of fire/explosion of hydrogen at subatmospheric pressures because a nonflammable mixture at atmospheric pressure becomes flammable at lower pressures. The significance of the increased risk requires a detailed risk analysis and depends on the particular process conditions and operation; nevertheless, more care should be taken when handling hydrogen at subatmospheric pressures.

Combined with the obtained UFL in an earlier study,<sup>7</sup> the flammable region of hydrogen expands when the initial pressure increases from 0.1 to 0.3 atm. The region is the widest at 0.3 atm where the UFL increases by 2.1 mol %<sup>7</sup> and the LFL decreases by 0.2 mol %. The flammable region starts to narrow when the pressure increases from 0.3 to 1.0 atm. Studies with a hydrogen flammability limit at high pressures showed that the flammable region continued to narrow when the initial pressure increased from 1.0 atm to as much as 10 atm, and then the region started to widen again with a further increase of pressure.<sup>33–37</sup> The narrowing of the flammable region of hydrogen at pressures from 0.3 to 1.0 atm in our studies and up to 10 atm in others can be explained by a hydrogen combustion reaction mechanism where the influence of the three-body chain termination reaction,  $H + O_2 + M \rightarrow HO_2 + M$ , becomes stronger when the pressure increases, which results in a decreased rate of the overall combustion reaction, thus narrowing the flammable region.<sup>7,37–40</sup> Details about the effect of the three-body reaction on the hydrogen flammable region are reported in our previous study.<sup>7</sup>

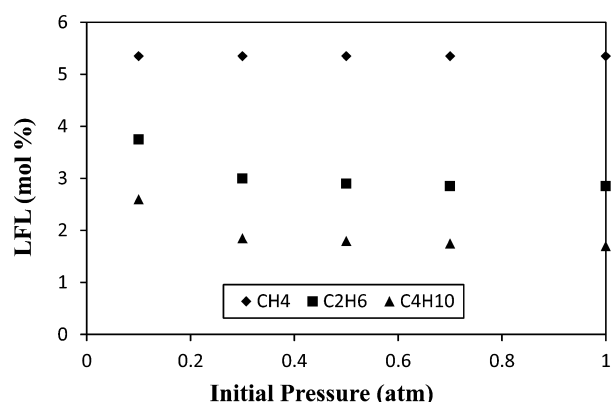
**Table 3. LFLs (mol %) and UFLs<sup>7</sup> (mol %) of Hydrogen and Light Hydrocarbons at Subatmospheric Pressures and Room Temperature<sup>a</sup>**

P (atm)	H <sub>2</sub>		CH <sub>4</sub>		C <sub>2</sub> H <sub>6</sub>		C <sub>4</sub> H <sub>10</sub>		C <sub>2</sub> H <sub>4</sub>	
	LFL	UFL	LFL	UFL	LFL	UFL	LFL	UFL	LFL	UFL
1.0	3.95	75.73	5.35	15.40	2.85	14.00	1.70	8.46	2.85	30.61
0.7	3.85	75.88	5.35	14.85	2.85	13.64	1.75	8.33	2.90	29.49
0.5	3.85	77.30	5.35	14.65	2.90	12.86	1.80	8.18	2.95	27.50
0.3	3.75	77.80	5.35	14.50	3.00	12.37	1.85	8.10	2.95	23.39
0.1	4.14	76.95	5.35	14.35	3.75	11.76	2.60	8.08	3.45	19.26

<sup>a</sup>Maximum uncertainty: 0.15 mol %

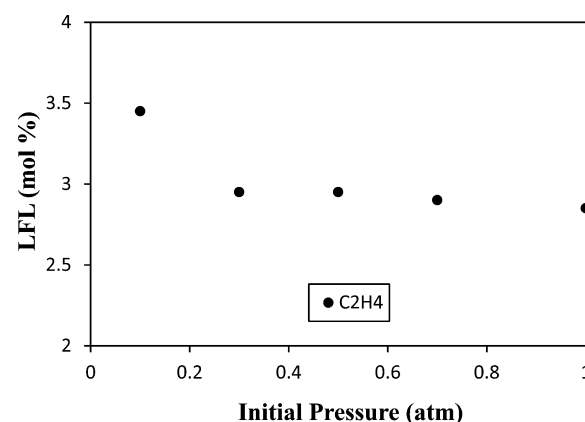
Under the influence of pressure, the change of the LFL was observed to be less than that of the UFL.<sup>7</sup> For example, when the initial pressure decreased from 1.0 to 0.1 atm, the maximum change of the LFL was 0.2 mol %, which is much smaller than that of the UFL which was 2.1 mol %.<sup>7</sup> Research on the flammability limit of hydrogen at high pressures (greater than 1.0 atm) also showed a greater impact of pressure on the UFL.<sup>35,36</sup> Terres and Plenz observed that the change of the UFL was 2 times larger than that of the LFL when the pressure increased from 1.0 to 10 atm.<sup>36</sup> Experimental results by Bone et al. showed that the LFL was almost unaffected when the pressure increased from 1.0 to 125 atm, while the UFL progressively increased with pressure greater than 10 atm.<sup>35</sup> Shebeko et al. also found a negligible influence of pressure on the LFL at a high pressure range from 2.0 to 4.0 MPa.<sup>37</sup> The reason for the higher impact of pressure on the UFL is currently unclear. We believe that a study into the reaction mechanism of hydrogen at limiting concentrations (UFL and LFL) under the influence of pressure may find an explanation for this phenomenon, which will be our focus in the future.

**3.3. Lower Flammability Limits of Methane, Ethane, *n*-Butane, and Ethylene in Air at Subatmospheric Pressures.** The obtained LFLs of the hydrocarbons in air at subatmospheric pressures and room temperature are summarized in Table 3. UFLs of the hydrocarbons determined at the same conditions as those in an earlier study<sup>7</sup> are also included for complete information about the flammability regions of the fuels. To better illustrate the behavior of the LFLs, Figure 3 and



**Figure 3.** Lower flammability limits of methane–air, ethane–air, and *n*-butane–air at subatmospheric pressures and room temperature.

Figure 4 were constructed for the alkanes and ethylene, respectively. Again, for conciseness and clarity, error bars are not included in these figures. Overall, the LFLs of the hydrocarbons increased when the initial pressure decreased from 1.0 to 0.1 atm, except for methane where the LFL did not change with pressure. The increase of the LFLs was small when the pressure decreased from 1.0 to 0.3 atm, and then the LFLs started to increase abruptly when the pressure was further reduced to 0.1 atm, except for methane. The reason why the LFL of methane behaves differently from those of other alkanes and ethylene under the influence of pressure is not clearly understood at the moment.<sup>1,35,37,41,42</sup> The distinctive molecular structure of methane, which does not contain any C–C bond, is a possible reason for the difference in LFL behavior from that of C<sub>2</sub> and higher hydrocarbons.<sup>38</sup> However, to provide a clear explanation, a careful study into the reaction mechanism of methane under the influence of pressure should be performed



**Figure 4.** Lower flammability limit of ethylene–air at subatmospheric pressures and room temperature.

(this will be a focus of our future studies). As for the reason why the LFLs changed abruptly when the pressure was further reduced to 0.1 atm, it has been observed that the initial pressure has little effect on the LFL until at certain low pressure where the combustion reaction rate is greatly reduced from the decreased collision frequency of reactive species.<sup>1,3,38,43</sup> This results in a sudden narrowing of the flammable range; therefore, a sudden increase of the LFL is observed. Our results indicate that 0.1 atm is the starting point where the influence of pressure on the combustion reactions of hydrogen and the hydrocarbons become stronger, resulting in the abrupt change in the LFLs.

Compared to the changes of the UFLs determined earlier,<sup>7</sup> the changes of the LFLs were much smaller. For example, when the pressure was reduced from 1.0 to 0.1 atm, the LFLs of all the hydrocarbons increased within 0.9 mol % while the UFLs decreased much more drastically which was as much as 11.35 mol % for the ethylene case.<sup>7</sup> Previous studies with flammability limits of the hydrocarbons at pressures higher than 1.0 atm also showed a greater impact of pressure on UFL than on LFL.<sup>1,2,41,42,44–46</sup> For instance, Kondo et al. experimented with methane in a spherical apparatus and observed that the LFL was almost unchanged when the pressure increased from 1 to 25 atm while the UFL increased rapidly with pressure.<sup>41</sup> The same observation was made by Hertzberg et al. for methane LFL at pressures from 1 to 3 atm.<sup>42</sup> For ethane and *n*-butane, data from the Bureau of Mines<sup>1</sup> show greater change in the UFLs compared to the LFLs in the pressure range from 1 to 6 atm. For ethylene, Craven et al.<sup>45</sup> observed that the LFL was almost constant while the UFL increased drastically when the pressure increased from 1 to 10 atm. Similar to the discussion in the previous section on the LFL of hydrogen, the reason for the greater impact of pressure on the UFLs of the hydrocarbons is not clearly understood at the moment. A thorough investigation into the reaction mechanisms of the hydrocarbons under the influence of pressure may provide an explanation for this observation.

For the alkanes, when the pressure decreased from 1.0 to 0.1 atm, the behavior of the LFLs did not follow any clear pattern (Figure 3) as opposed to the UFLs which decreased linearly with pressure as observed in our previous study.<sup>7</sup> As shown in Figure 3, *n*-butane has the lowest LFL at all initial pressures followed by ethane and methane; in other words, the higher the carbon number (or molecular weight), the lower the LFL. This molecular weight–LFL relationship of alkane hydrocarbons was



also observed in other studies at atmospheric pressure.<sup>2</sup> The trend is the same for the UFL as observed in our previous study:<sup>7</sup> the higher the carbon number, the lower the UFL; for example, *n*-butane had the lowest value of UFL followed by ethane and methane.

Note that for ethylene, while the UFL changed significantly with pressure as observed in an earlier study,<sup>7</sup> e.g., the UFL decreased by 7.2 mol % when the pressure decreased from 1.0 to 0.3 atm,<sup>7</sup> the LFL did not show any appreciable change even at a pressure as low as 0.3 atm (Figure 4). It was explained in our earlier study<sup>7</sup> based on the reaction modeling work of Carriere et al.<sup>47</sup> that the great impact of pressure on the UFL of ethylene was due to the high sensitivity of the combustion reaction mechanism of fuel-rich mixtures of ethylene to changes in the pressure. Therefore, on the basis of the observed behavior of the LFL, it is assumed that pressure does not have much impact on the reaction mechanism of lean mixtures of ethylene; however, to confirm this assumption, a study similar to that of Carriere et al.,<sup>47</sup> on the reaction mechanism modeling for lean mixtures of ethylene, should be performed.

Combined with the obtained UFLs of the hydrocarbons in our earlier study where the UFLs decreased with pressure,<sup>7</sup> the flammable regions of the hydrocarbons narrow when the pressure decreases below 1.0 atm. When the pressure increases above 1.0 atm, the regions expand as observed in various studies.<sup>1,41,45,48</sup> Therefore, it can be concluded that the flammability regions of the hydrocarbons become smaller when the initial pressure decreases, both at low and high pressure regimes. From an inherent safety point of view where the principle is to avoid hazards instead of controlling them, a process is inherently safer if is designed in such a way that it relies on chemistry and physics to prevent accidents rather than on control systems, interlocks, redundancy, etc.<sup>3,49</sup> Therefore, operating under a condition where the hazards of the materials are reduced or avoided is one important approach to inherently safer process design.<sup>49</sup> On the basis of the results of this study, to reduce the risk of fire and explosion of the hydrocarbons or to be inherently safer, it is recommended that the operating pressure is reduced as much as possible. This may not be the case for hydrogen because its flammability region widens with decreasing pressure from 1.0 to 0.3 atm; therefore, the safe operating pressure for hydrogen needs to be identified based on the specific operating system.

**3.4. Adiabatic Flame Temperatures of Hydrogen and the Hydrocarbons at LFL Concentration and Subatmospheric Pressures.** Adiabatic flame temperatures are calculated based on the assumption of no heat loss and that the system reaches chemical equilibrium.<sup>38,50</sup> In this study, the adiabatic flame temperatures (AFTs) of hydrogen and the hydrocarbons at the LFL concentrations of the chemicals, room temperature, and subatmospheric pressures were calculated using the EQUILIBRIUM program in CHEMKIN package.<sup>17–19</sup> The thermodynamics properties and species data files were obtained from the database of Kee et al.,<sup>18,19</sup> GRI Mech 3.0 files<sup>20</sup> (for hydrogen, methane, ethane, and ethylene), and Combustion Chemistry Center's<sup>21</sup> *n*-butane mechanism (for *n*-butane). Note that the AFTs in this work were calculated under a constant volume condition which agreed with the experimental setup, in which the LFLs were measured in a closed cylindrical vessel. Constant volume AFT is generally higher than constant pressure AFT because no energy is utilized to change the volume of the system or generate work.

Table 4 summarizes the calculated AFTs of hydrogen and the hydrocarbons at the obtained LFL concentrations of the

**Table 4. Calculated Adiabatic Flame Temperatures (at constant volume) of Hydrogen and Hydrocarbons in Air at LFL Concentration, Room Temperature, and Subatmospheric Pressures**

initial pressure (atm)	adiabatic flame temperature (K)				
	hydrogen	methane	ethane	<i>n</i> -butane	ethylene
1.0	734	1898	1815	1942	1744
0.7	722	1898	1815	1964	1771
0.5	722	1897	1839	2008	1771
0.3	714	1897	1885	2028	1771
0.1	743	1894	2149	2409	1967

chemicals, room temperature, and subatmospheric pressures. Overall, the behavior of the AFTs under the influence of pressure was similar to that of the LFLs. For example, the AFT of hydrogen decreases with pressure from 1.0 to 0.3 atm and then increases with the further decrease of pressure; the same was observed with the LFL (section 3.2). For the hydrocarbons, similar to the behavior of the LFLs (section 3.3), the AFTs increase when the pressure decreases, except for methane where the AFT does not change much with pressure. For both hydrogen and the hydrocarbons, the changes of the AFTs under the influence of pressure are small as also observed with the LFLs. These similarities are understandable because at LFL concentration, fuel is the limiting reactant (oxygen is in excess); therefore, the heat of combustion is proportional to the amount of fuel reacted which is the LFL concentration. The heat of combustion is then consumed to raise the temperature of the products to its AFT; thus, AFT is proportional to heat of combustion which makes it proportional to the LFL and explains the similarities between the two under the influence of pressure.

On average, at initial pressure from 1.0 to 0.1 atm and LFL concentration, the AFT of hydrogen is about 730 K, and the AFTs of the alkanes and ethylene are 1900 K and 1800 K, respectively. From a safety point of view, this much lower AFT of hydrogen suggests a smaller thermal impact, hence a smaller consequence severity, of a fire involving hydrogen at lean concentration, whereas the impact of a hydrocarbon fire can be significantly higher because of their high AFTs. However, the risk of a hydrogen fire at lean concentration should not be ignored because its thermal radiation could be high enough to ignite other fuels which have low ignition temperatures (e.g., gasoline,<sup>4</sup> acetylene<sup>2</sup>) if the fuels are stored nearby, resulting in much more severe consequences. Therefore, the risk of fire/explosion of hydrogen should be carefully analyzed not only based on the concentration of hydrogen but also on other factors such as the operating condition, proximity to other fuels, etc.

#### 4. CONCLUSION

The lower flammability limits (LFLs) and adiabatic flame temperatures (AFTs) at LFL concentrations of hydrogen, methane, ethane, *n*-butane, and ethylene were determined at room temperature (20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, and 0.1 atm. The LFL of hydrogen initially decreased when the pressure was reduced from 1.0 to 0.3 atm, and then the LFL increased with the further decrease of pressure. Under the influence of pressure, the LFL of hydrogen changed less than

the UFL;<sup>7</sup> the maximum change of the LFL was 0.2 mol % while the maximum change of the UFL was much larger, which was 2.1%<sup>7</sup> when the initial pressure decreased from 1.0 to 0.1 atm. Combined with the value of the UFL generated in the previous study,<sup>7</sup> the flammable region of hydrogen widened when the pressure decreased below 1.0 atm. The region was the widest at 0.3 atm and started to narrow when pressure decreased below 0.3 atm. This behavior suggests the increased risk of fire/explosion of hydrogen at subatmospheric pressures; thus, more precaution is recommended when handling hydrogen at low pressure conditions.

In contrast to the behavior of the LFL of hydrogen, the LFLs of the hydrocarbons increased when the pressure decreased from 1.0 to 0.1 atm, except for methane where the LFL did not change with pressure. Compared to the changes of the UFLs of the hydrocarbons determined earlier,<sup>7</sup> the changes of the LFLs were much smaller, which suggests a smaller impact of pressure on the LFLs. Combined with the values of the UFLs,<sup>7</sup> the flammable regions of the hydrocarbons narrowed when the pressure decreased; thus, from an inherent safety point of view, it is recommended to handle these hydrocarbons at a pressure as low as possible.

Under the influence of pressure, the behaviors of the AFTs of hydrogen and the hydrocarbons at the LFL concentrations of the chemicals were similar to those of the LFLs. For example, the AFT of hydrogen decreased with pressure from 1.0 to 0.3 atm and then increased with a further decrease of pressure; the same was observed with the LFL. For the hydrocarbons, the AFTs increased when the pressure decreased, except for methane where the AFT did not change much with pressure. For both hydrogen and the hydrocarbons, the change of the AFTs with pressure was small as also observed with the LFLs.

On average, at initial pressures from 1.0 to 0.1 atm and LFL concentration, the AFT of hydrogen was much smaller than that of the hydrocarbons: the AFT of hydrogen was about 730 K, while the AFTs of the alkanes and ethylene were 1900 K and 1800 K, respectively. This suggests a less severe consequence (smaller thermal impact) for hydrogen at low pressures and at LFL concentration; however, the risk for hydrogen should not be ignored because it depends on many other factors, such as the probability of ignition, the proximity to other fuels, etc.

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### Notes

The authors declare no competing financial interest.

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