

Flame Front Model with the Clusters Condensation

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Abstract. The processes model in a flame during the n-alkanes air mixture combustion initiation is proposed, taking into account the supramolecular structures formation possibility in the peroxide clusters form. This approach is justified by the n-alkanes melting temperatures correlation with their autoignition temperatures and anti-knock indexes. The condensation possibility is provided for such high molecular structures. Boiling temperatures values at flame front pressures characteristic were evaluated. To predict the peroxide clusters melting temperatures, a formula developed earlier for the hydrocarbons condensed state was used, which takes into account the length and molecular weight of modeled clusters. Expected peroxide clusters melting temperatures were predicted for conditions of dimeric and tetrameric structures. A linear dependence was used to recalculation the obtained values in boiling temperatures. It is shown that the calculated clusters phase transitions characteristic temperatures can be realized in the flame front preparatory zone. Based on the condensation theory, the flame front thickness and the minimum non-extinguishing sphere radius during ignition were estimated: the obtained data closely coincide with these parameters known values.

Introduction

Flame combustion developmental processes are explained by several theories within their paradigms [1]. The thermal theory treats the combustion process as a "black box", the input and output parameters for which are the material and energy balances components in a generalized form; it does not take into account the chemical transformations mechanisms, but considers the certain processes heat accumulation possibility. The peroxide theory takes into account the oxidation intermediate stages presence in the peroxide compounds formation form, which is observed in the flame; but the proposed phasing contradicts the combustion reaction high speed. The chain theory additionally predicts the free radicals formation in hydrocarbon oxidation processes, which have sufficient energy to activate the next molecule with the formation of more than one flame active center, which causes the reaction paths branching and its acceleration. But radicals are already products of some reaction, that is, the theory does not describe the flame initiation mechanism except in the case of ignition by an electric discharge, when ions become primary active centers. That is, there is a need to formulate a generalized explanation regarding the first elementary act, which leads to the next chemical equilibrium shift in the system.

Some researchers predict the quasi-liquid formation in the flame, which at the molecular level forms nanopores, in walls of which significant pressures are formed with the molecules emission possibility, shock ionization, which initiates the detonation combustion [2]. Nanopores are separated by the molecules double layer: this is similar to the foam structure, where the walls have some properties of a solid. According to a similar mechanism, seam detonation in coal nanopores with the methane release in quantities greater than the pores volume is also predicted [3, 4]. But the

authors do not consider the peroxide complexes formation stage, that shown by some studies on the coal spontaneous combustion [5]. Intermediate peroxide compounds are also formed during the oiled materials spontaneous combustion. Then the peroxide complexes formation can be the combustion initiation first stage. At the same time, complex compounds are heavier than original molecules, so they will have easier conditions for the condensation into a quasi-liquid. This quasi-liquid has certain melting points t_{mp} and boiling points t_{bp} . This creates the film formation hypothetical possibility of combustible liquid or its peroxide complexes in the flame front.

Thus, this study task is to model possible supramolecular peroxide structures, establish possible conditions for their condensation, model the corresponding processes accompanying combustion.

Literature Review

Substance condensed state properties are determined by the intermolecular interaction presence. But this influence level is often taken into account indirectly. Liquids modeling and their properties is carried out on the molecules coarse-grained model basis within the statistical associative theory by replacing the molecule with a solid balls limited number, by which fill the matrices [6], that allows predicting many substance properties and internal force fields. But such a model has a discrete evaluation and does not describe short molecules, as well as the supramolecular structure.

The strongest intermolecular interaction is manifested in the solid state; upon transition to the liquid state, the clusters are deformed [7]. The "cluster" concept was originally used for metals, which clusters stabilize by ligands, which is similar to the hydrogen role near the molecules hydrocarbons carbon skeleton. But t_{mp} of hydrocarbons and metals do not show a common dependence, even if we rely on the clusters molecular weight [8]. At the same time, the metal nanoclusters t_{mp} is kelvins tens, which is close to the short hydrocarbons t_{mp} [7]. The discrepancy in dependences can be connected with the clusters different structure: Au₂₀ tetrahedral lattices [9] have an edge size of "4", and the n-hexane dimer has a framework length of "12".

It is known that alkenes substitution reactions occur through the complex compound formation stage with a substituent at the electron density change place [10, 11]. In alkanes, methyl final groups create an induction effect, then the changes greatest intensity in the electron density redistribution is observed on the second frame carbon. But this effect will become noticeable only starting with pentane, which will have a molecule average region with a constant electron density. There is a possibility of molecules pairs clustering by the second carbon position in the chain, depending on the "even-odd" for molecules due to the interaction valence angle presence and their different complementarity. Therefore, hydrocarbons many parameters have pulsating deviations from a smooth dependence. This is most noticeable for t_{mp} with a separate anomaly for methane and ethane (increased t_{mp}), and it is taken into account by the cyclic hexameric structure for methane, trimer structure for ethane, dimer structure for following alkanes [12]. This assumption is indirectly confirmed by the fact that the methane flash point t_{fp} is lower than t_{mp} , which is characteristic for cyclic compounds – benzene, cyclohexane, methenamine [13]. The extinguishing substances consumption to stop the liquids burning is determined by t_{fp} , but the cluster length of the hydrocarbon that burns is more precisely modulated by such selection [14].

For the gaseous state, the intermolecular interaction should be less pronounced, therefore the dependence step anomalies for the t_{ai} n-alkanes cause misunderstandings [15]. But there is this dependence fundamental similarity to the n-alkanes water solubility γ [13]. Then it is possible to make assumptions about fundamentally identical supramolecular structures during the combustion initiation and dissolution in water. Dissolution in water involves the associates formation, accordingly, at the autoignition moment, there is a n-alkanes "quasi-dissolution" in an oxygen-containing environment. Supramolecular structures are formed with the oxygen molecules participation, which are further transformed into intermediate peroxide compounds. For methane, ethane and propane, clusters at the melting moment contain the same carbon atoms number "6", but methane and ethane clusters are slightly heavier due to additional hydrogen atoms, so their t_{mp} is several degrees higher than has propane. The somewhat understated t_{ai} of methane and ethane can be explained similarly [13]. That is, alkanes with clusters of the same length and the same molar mass will have

the same value of γ , t_{mp} or t_{ai} . It notes the fact that for n-alkanes, starting from dodecane, t_{mp} becomes greater than t_{ai} . In this region, t_{ai} stops decreasing, stabilizes, begins to increase somewhat.

The dependences similarity t_{ai} and anti-knock index AKI, which also has pulsations, was also noted [15]. In an indirect way, the clustering theory in the flame is confirmed by the certain correlation existence between such various parameters as t_{mp} , t_{bp} and t_{ai} : linear dependences with correction for the carbon atoms number for n-alkanes $t_{ai} = |t_{mp} - 355 + 5n_c|$ with $R = 0,82$; $t_{ai} = |t_{bp} - 360 - 10n_c|$ with $R=0,9$ ($^{\circ}\text{C}$). The best description by linear dependence was obtained for AKI: $\text{AKI} = -0.77t_{mp} - 35$ with $R = 0.968$; at the same time, the largest errors are observed for butane, heptane, and octane, which may indicate a difference in the clusters structure at the melting moment and in the flame. That is, t_{mp} can act as an intermolecular interaction presence indicator for the flame.

We accept the model that during evaporation n-alkanes go into a monomolecular state, during condensation they dimerize [12]. If we expect the peroxide clusters dimerization during condensation, then this process characteristic temperatures will be different from those characteristic of starting alkanes. The peroxide groups presence additionally increases the molecular weight and length of the cluster, which should be manifested in the growth of t_{mp} and t_{bp} . Considering the fact that the peroxide clusters molecular mass will be more than twice as large, condensation processes will occur much more easily. In addition, condensation processes can be further facilitated under high pressures conditions in the flame front. But at the same time, the temperature also increases in this area, which will interfere with the condensation. Condensation will occur if the pressure increase is more intense than the temperature increase.

Autog ignition can be considered as the combustion occurrence simultaneously in the entire heated volume at certain temperatures and pressures. Then the flame propagation speed will be the speed of the organization cooperative process of the continuous supramolecular structure. At this moment, elevated pressures are not yet formed. In this case, t_{ai} is the temperature at which the bulk peroxide cluster formation capable of the condensation occurs. That is, t_{ai} at the combustion initiation moment performs the role of t_{mp} for the peroxide structure, which is further destroyed. Yes, it is known that dimethyl peroxide explodes at the crystallization moment, other organic peroxides - at the boiling moment [10, 16]. Further processes develop according to radical mechanisms according to the chain reactions theory [1].

Thus, under high pressures in the flame front, either the combustible substance or its peroxide clusters can condense; at the same time, we can talk about the presence of a mixture certain critical temperature, at which a clustering cooperative process occurs with the peroxide complexes formation without increasing pressure. Therefore, to characterize the combustion occurrence, it is necessary to operate with the lengths and molecular masses values of clusters. We developed the corresponding dependence for the melting process [15].

Materials and Research Methods

Alkanes are the hydrocarbons best-studied class, so they were chosen as the basis for supramolecular structures building models and conducting calculation studies. The modeling starting principle is that corresponding clusters of solid and liquid states, conditions of the autoignition and dissolution in water should have a certain similarity. We predicted that clusters with the same length n_{Ceq} and molecular mass M should have the same t_{mp} [15]:

$$t_{mp} = 101.85 \ln(n_M) - 452.37, \text{ } ^{\circ}\text{C}, \quad (1)$$

where n_M is the "melting ease" indicator, $n_M = n_{Ceq} M^{0.2}$.

Although formula (1) was developed for hydrocarbons, but if for the Au_{20} cluster the modulating size is chosen not the edge length "4", not the atoms number "20", but "4000", then t_{mp} simulation can be ensured. The factor of 200 to the atoms number determines the electron density redistribution total path in the crystal (in contrast to the hydrocarbons linear structure). But the inverse

proportionality to the molecular weight of the ternary alloy smallest clusters was invented for the alloys microhardness [7]. An attempt to improve the correlation by taking into account the cluster length showed that it is sufficient to take into account the its edge size. That is, some substance physical and chemical properties are determined by the electron density redistribution, and for some, the cluster external size works as an indicator of the intermolecular interaction elasticity.

There is a linear relationship between t_{mp} and t_{bp} of n-alkanes [17]:

$$t_{bp} = t_{mp} + 9,8992n_C + 109,89, \quad (2)$$

where n_C is the carbon atoms number in the n-alkane molecule.

But formula (2) does not take into account the pulsation differences between t_{mp} and t_{bp} , does not work for methane and ethane, but works for their peroxide clusters.

Regarding the condensation possibility assessment of combustible substance clusters in the flame front, we assume that the peroxide cluster dimer formed in the combustible mixture will condense under certain circumstances. Then, according to equation (1), its t_{mp} can be estimated, while for many combustible substances such a condensed cluster will be a combustible substance molecule tetramer analogue. In addition, in the equivalent length and molar mass, it is necessary to take into account a oxygen atoms certain number that could be cluster part as peroxide groups.

Data on the substance physical and chemical properties were selected from international reference systems [11, 18].

Research Results

For the flame front propagation and for the combustion initiation by the electric discharge, one can imagine such these processes initial stage, when hot zone fast molecules already create pressure on cold zone molecules in the nanolayer, but have not yet mixed with it. In the compressed nanolayer, the combustible substance condensation possibility in the form of combustible substance molecules dimers or peroxide clusters dimers is created. The substance condensed state formation correlates with the changes pulsating nature in n- some parameters of the alkanes fire hazard [19, 20]. Pulsation of t_{fp} for n-alkanes is most likely determined not so much by the evaporation process from the condensed state, but by cluster formation at the ignition time.

Peroxide clusters are more massive structures than the n-alkanes original molecules, so they will have higher phase transitions characteristic temperatures t_{mp} and t_{bp} , which can create conditions for condensation processes in the flame front. If the combustion initiation first stage is the condensation process of the combustible substance itself, then at the next stage aggregation with oxygen will take place as a heterogeneous process. By analogy with the solubility limit, there are critical ratios in the mixture between the combustible substance and oxygen, at which the combustible substance aggregates all oxygen according to a certain scheme. The aggregation mechanism also determines the values of combustion limits: LEL–UEL, LFL–UFL.

Consider the compression conditions effect on the change in t_{bp} of n-hexane C_6H_{14} with the pressure increase in 10 times from the standard one, which is typical for combustion processes. According to Antoine's equation [16], with such the pressure increase, t_{bp} increases by 100 °C, that is, $t_{bp} \approx 168$ °C. If it compares, n-decane $C_{10}H_{22}$ has a close t_{bp} : $t_{bp} \approx 174,1$ °C [13]. According to the data for n-decane, one can expect for n-hexane at a pressure of 1000 kPa an increase in t_{mp} to approximately "-30 °C", that is, by 65 °C.

As was mentioned for peroxide clusters, additional dimerization under condensation conditions will form tetramers in relation to the combustible substance monomolecular state with two additional peroxide groups. Then the condensed peroxide cluster framework length, taking into account the peroxide groups, will be as follows $n_{Ceq} = 6 \cdot 4 + 2 \cdot 2 = 28$, which for the condensed state corresponds to the n-tetradecane dimer length with $t_{mp} = 5,9$ °C and $t_{bp} = 253,7$ °C.

But for the stoichiometric concentration for the all oxygen molecules aggregation, the cyclic tetramer model with two peroxide groups works, as well as with four peroxide groups for the polymerization with similar clusters (that is, for one such peroxide monomer there are 2 additional peroxide groups). Then the equivalent length under the condensation conditions of such a peroxide cluster will be $n_{C_{eq}} = 6 \cdot 8 + 2 \cdot 4 = 56$, which for the condensed state corresponds to the dimer length n-octacosane with $t_{mp} = 61$ °C and $t_{bp} = 432$ °C. Such temperatures occur in the flame front preparatory zone, so condensation processes are possible.

The expected t_{mp} of the predicted alkanperoxide clusters can be estimated from formula (1), which relates the t_{mp} to the cluster length and its molecular weight. There is a fundamental linear relationship between t_{mp} and t_{bp} of n-alkanes, which is described by the Eq. (2). The calculations results for peroxide dimers (model No. 1) and tetramers (model No. 2) are shown in Fig. 1, where it is also taken into account as an option for the flame structures that at the melting moment methane is as the hexamer, ethane is as the trimer. For comparison, Fig. 1 shows the t_{mp} and t_{bp} of the n-alkanes monomolecular state. For peroxide clusters, at this research stage, the shortened clustering schemes, which describe the pulsatility of t_{mp} n-alkanes, were not applied.

The well-known phenomenon of alkyl peroxides and cycloperoxides formation at intermediate stages of the combustion processes development can be considered as a consequence of peroxide dimerization of the n-alkane molecule by association with air oxygen. The larger clusters length and molar mass determines the growth of t_{mp} and t_{bp} . But for the methane solid state, we previously proposed a hexameric structure in contrast to other n-alkanes [12, 17], therefore, the dependence for peroxide dimers alkanes also shows a possible characteristic temperature for methane as for the hexamer, for ethane as for the trimer, Fig. 1. This correlates with the well-known fact that methane is less prone to detonation than propane at normal pressures, and more prone to detonation at higher pressures. Then, during methane detonation under increased pressure conditions, it can talk about the quasi-solid substance formation with hexameric clusters in the flame front. If it considers the possibility of the formation of alkanes polymer-like peroxide clusters with a higher coordination number, then corresponding characteristic temperatures will be even higher.

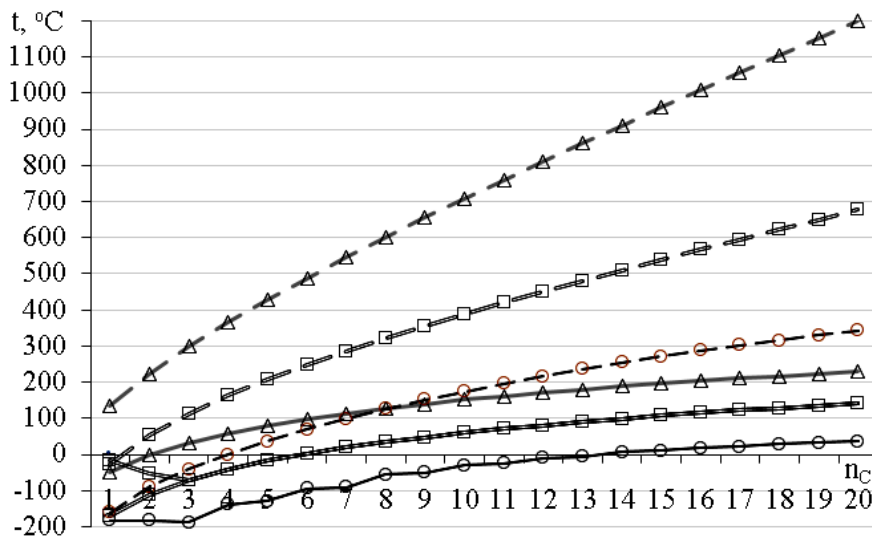


Fig. 1. Temperatures of n-alkanes phase transitions "o", their peroxide dimers (or hexamer for methane, trimer for ethane) "□", peroxide tetramers «Δ»: — — — t_{mp} , — — — t_{bp} .

The dew point temperature for the hydrocarbons stoichiometric concentration is about 80% of t_{bp} calculated in "K", which for n-alkanes ($n_c=1-20$) peroxide dimers is "-80–400" °C, for tetramers – "300–900" °C. If clustering occurs at temperatures in the flame preparation zone lower than the dew point, the clusters will condense. Thus, for different temperatures, pressures and combustible substance concentrations, there may be transition different schemes to the condensed state. In the peroxide tetramers state of n-alkanes (model No. 2, Fig. 1) in the deflagration flame preparatory zone, the peroxide clusters transition to a quasi-liquid state is possible for all n-alkanes, and the crystallization starts with propane. The increased pressure presence facilitates these processes.

Thermal theory explains the zones structure of the kinetic flame by the fact that the combustion zone begins where the preparation zone temperature reaches t_{ai} . It can be expected that at this temperature the n-alkanes peroxide clustering with the condensation occurs. This assumption explains the lower t_{ai} of long hydrocarbons, since they have simpler conditions for the condensation.

An analogy can be drawn between the combustion occurrence and the crystals nucleation: more energy is needed to initiate a crystal than to continue its growth [21]. The process can be called autocatalytic, and its speed increases in the proportion to the outer surface development. It is possible to consider a model according to which the flame front propagation from an ignition point source occurs according to the principle of the sequential growth of supramolecular structure new layers, but previous layers are immediately destroyed and form a combustion zone. For example, there is a self-propagating high-temperature synthesis phenomenon [22], during which such clustering products do not destroy in the combustion front.

If the condensation occurs in the flame, it is possible to estimate – which air combustible mixture layer can ensure the single monomolecular film formation. The difference in liquid and gaseous states densities is approximately 1000 times. Then a combustible liquid monomolecular film will form about 1000 layers of molecules during evaporation, which is about 0.001 mm. Methane requires 9.52 moles of air for the 1 mole combustion, for longer n-alkanes this number decreases to 7.3 per one molecular link. Then we can conditionally assume that the combustible mixture minimum layer, which is necessary for the solid film formation, will be 10 times larger, that is, 0.01 mm, which coincides with the known value of the flame front thickness.

Under combustion initiation conditions by an electric spark, a certain spherical volume of a heated combustible mixture should be sufficient for the formation of a combustible substance monomolecular film on its surface. In addition, it should be borne in mind that the electric discharge place is characterized by the molecular structure destruction and the plasma formation, so this volume part will not participate in condensation processes. But this sector outer surface is 5.4 times larger than the frontal surface of the combustible system cubic element with a face of 0.01 mm. That is, the sphere volume with a radius of 0.0125 mm is not yet sufficient for the continuous film formation on the outer surface. This condition fulfillment is provided by the sphere with a radius of 0.03 mm, which is three times the flame front thickness. Taking into account the internal plasma region presence, this proportionality will be greater than "3". In practice, it is said that the minimum non-extinguishing sphere radius should be 3.7 times greater than the flame front thickness [1].

We can offer 4 options for initiating combustion and spreading the flame front: 1) when t_{ai} is reached in the entire combustible mixture volume, a n-alkanes peroxide clustering cooperative process of with condensation in the spongy film structure form occurs; 2) clustering volumetric process with the combustible substance condensation or its peroxide clusters as a combustible mixture compression result; 3) under conditions of the deflagration combustion propagation at a certain temperature, a solid film is formed in the flame front interlayer as a result of the n-alkanes peroxide clustering with condensation; 4) under conditions of the detonation combustion propagation under a certain pressure in the flame front layer, the clustering process with combustible substance condensation or its peroxide clusters is initiated.

Peroxide clusters become an intermediate unstable form of the combustible substance molecules existence. Condensation processes occur with the heat release, which can be a determining factor for the combustion initiation completion. During the fires occurrence simulation, temperature fluctuations are noted [23], which are explained by the fractal structures occurrence [24]. In the detonation flame front of a stoichiometric combustible mixture, the free carbon appearance of anisotropic and amorphous structures is recorded [2], as well as the shock waves propagation in the flame front plane, the retardation and acceleration stages of the flame front near a certain velocity. Processes of the n-alkanes peroxide clustering with the condensation may require an excess amount of oxygen relative to the combustion process balance, accordingly, inhomogeneities in the form of enriched and depleted regions will appear in the flame front. Anisotropic, diamond-like structures can be formed through the stage of the hexameric methane clusters formation [12].

The liquid state is characterized by the surface tension presence. This can contribute to the formation in the flame front of a condensed clusters with the drop-like distribution, it is similar to an aerosol. Such a model also explains the enriched and depleted regions formation in the flame front. Then the each drop explosive combustion creates circular shock waves near it, which propagate both in the flame front direction and in its plane. Enriched regions after the explosion will contain the excess carbon after the combustible substance peroxide clusters decomposition. Combustible substance condensed peroxide clusters decomposition can be initiated by both the condensation process heat release and the flame front radiation.

Thus, we consider autoignition as combustible substance peroxide clustering with bulk condensation at the critical temperature or pressure; the deflagration flame propagation – as the film formation after the peroxide clusters condensate at the critical temperature; the detonation flame propagation – as the film (or aerosol) formation after the peroxide clusters condensate under the critical pressure. The transitional moment from the deflagration to detonation combustion is the pressure addition due to the fast molecules emission from the combustion zone to the cold mixture heating by the heat conduction mechanism. The gas-air mixtures detonation theory is based on the rapid adiabatic compression action, which heats and ignites the mixture without heating by the heat conduction [1]. But this approach does not describe well some cases of gas-air cloud explosions in the detonation mode [25]. The detonation description based on taking into account the condensation processes of peroxide clusters forms simplified requirements for achieving such a phenomenon. For example, the detonation initiation simplification is achieved by simultaneous or sequential paired spark discharge [26], which is used to create fire-fighting obstacles by a controlled explosion to limit fires in the open space, as well as to throw fire-extinguishing charges [27, 28]. The twin spark impact forms condensation inhomogeneities, which become the detonation flame front seeds with the formation of main and transverse shock waves.

For a diffusion flame, the n-alkanes peroxide clustering possibility in the flame preparation zone does not seem to exist. But, since there is incomplete combustion in the diffusion flame, it can be considered as continuing at the UEL with the corresponding supramolecular peroxide structures formation. Then the CO source in the incomplete combustion processes can be an alkyl peroxide group $-\text{CO}-\text{OC}-$. And CO detection is an important component of fires development analyzing, and the ability to control its formation is an important direction in the reducing the fires victims number [29].

This study results shed new light on the initiation and propagation combustion processes in deflagration or detonation modes and can be used to predict, model and detect the combustion or detonation development both in technological processes and during the occurrence and development of fires and explosions. The authors either did not describe or did not detect pressure reduction due to condensation processes in the nanosecond range [30, 31]. Extinguishing fires in ecosystems requires innovative approaches [32], extinguishing by the detonation explosion of gas charges has been investigated [33], that should occur through the condensation stage. Fire detection methods [34, 35, 36] can be investigated in the direction of condensed structures detection in the gas phase. For flame extinguishing according to the invented mechanism, it would be interesting to create a means that would form a non-flammable polymer-like mesh in the flame, similar to non-flammable fire-extinguishing gels [37].

Conclusion

The presence of peroxide clustering processes with the heavier supramolecular structures formation in the flame front at the combustion initiation stage is assumed. These structures have higher melting and boiling points. Then, in the flame front preparatory zone, condensation processes with the unstable polymer-like structure formation become possible. The implementing possibility such a model is indirectly confirmed by the correlation presence between the melting temperatures and anti-knock coefficient of n-alkanes with $R = 0.98$, thus the melting temperature acts as the intermolecular interaction presence indicator in the flame. The n-alkanes peroxide dimers model for $n_c = 1-20$ has expected melting temperatures of $-171-90\text{ }^\circ\text{C}$, boiling points of $-28-680\text{ }^\circ\text{C}$, dew points up to $400\text{ }^\circ\text{C}$. For methane melting moment, we previously proposed a hexameric model, which

provides the melting condition instead of "-170 °C" for the dimer – "-15 °C ". The n-alkanes peroxide tetramers model has expected melting points of "-49–180 °C ", boiling points of "130–1200 °C ", dew points up to 900 °C. Such temperatures can be realized in the flame front preparatory zone, and compression effects further facilitate the condensation processes. Based on such a minimum volume of the combustible air mixture, which is sufficient for the formation of a condensate continuous film from peroxide clusters on the sphere surface, the minimum non-extinguishing flame sphere radius, which is spreading capable, is determined, $3 \delta_{ff}$ (3 flame front thicknesses), which is slightly less than the known spark ignition rating of $3.7\delta_{ff}$. The difference is determined by the fact that in the electric discharge event, the middle zone of this sphere no longer contains the combustible substance molecules, which capable to the clustering by the peroxide mechanism, but contains the plasma. Thus, the substance peroxide clustering theory with the condensation allows us to describe the processes in the flame.

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