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A one-step conversion of propane and butane gas-fraction into methanol

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ABSTRACT

This study investigates the oxidative-conversion of propane-butane (C_3–C_4) fraction into methanol via a proposed vapor–gas system: $C_3–C_4 + O_2 + h\nu/HNO_3 \rightarrow 2CH_3OH + C_2H_4 + C_3H_6$. Experiments were performed by feeding propane-butane fraction, oxygen, and nitric-acid into a photo-chemical reactor under mild conditions at a temperature of 100^0C, an atmospheric pressure (P = 1 atm.),visible-light excitation at a wavelength $\lambda = 420$ nm, and under the influence of nitric-acid. The major products are methanol, ethylene and propylene.

Introduction

Methanol is not only a convenient liquid-fuel, but also, serves as a raw-material for chemical synthesis in the petroleum and petrochemical industries. Thereby, it is considered as one of the most-traded industrial chemicals, and an integral part of our economy with an annual production capacity of approximately 20 billion gallon [1**].**

The conventional technologies for methanol production involves steam-methane reforming (SMR) to syn-gas at a high temperature (T = 800 – 1000^0C) and moderate pressure (4 MPa) in [Eqn. (1)], followed by the conversion of syn-gas into methanol [Eqn. (2)] by passing it over co-precipitated copper/zinc-oxide (Cu/ZnO) catalysts at a low-temperature (T = 220 – 280^0C) and a high-pressure (P = 5 – 8 MPa) [2].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{f\,298} = +\,206 \text{ kJ/mol} \qquad (1)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H^0_{f\,298} = -\,90.7 \text{ kJ/mol} \qquad (2)$$

Notwithstanding, the overall-efficiency of methanol synthesis is greatly undermined by thermodynamics, and a high-theoretical conversion into carbon-monoxide (CO) [Eqn. (1)] due to the limitations imposed by the reaction-equilibrium and a low heat-efficiency. In addition to that, the applied high-temperature-and-pressure for the process lead to problems with the reactor materials, operation, and maintenance. Consequently, the existing commercial process for methanol production via the SMR is very energy-intensive, exhaustive, and not cost-effective [3]. Therefore, to significantly minimize the methanol production capital-cost (inherent of steam-reforming stage), an economically-feasible one-step methane conversion into methanol has long been suggested as an attractive option. The direct partial oxidation of methane into methanol [Eqn. (3)] is an exothermic reaction that is energetically more-efficient, tends to minimize temperature-and-pressure fluctuations, decreases the second-law efficiency losses, and can give quite good results than the endothermic (SMR) steam-methane reforming reaction [4]. Nevertheless, it is operated by a free radical mechanism which is hard to control [3–4, 6–10].

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH \quad \Delta H^0_{f\,298} = -\,126.4 \text{ kJ/mol} \qquad (3)$$

Even though, encouraging results have been obtained at the laboratory scale: for instance several works reported significantly higher methanol selectivity up to 80 % [5 – 6], and even > 90 % [7] past and recent effort to obtain competitive selectivities and yields of methanol that can be reproduced at the industrial level have been met with failure resulting into poor methane conversion (not *higher than* 5 %), a low methanol selectivity (not *exceeding* 50 %), and thereby, poor yield [9 – 10].

The reason for the unflagging interest and/or why the DMTM process is poorly promoted is twofold: On the one hand, a substantial amount of natural gas is inconveniently located, and there is currently no safe and economically viable method in place for its transportation. On the other hand, it has been explicitly observed that under certain conditions (for instance at high-temperatures, the oxidation of even simple hydrocarbons, such as methane, is accompanied by a rapidly increasing-complexity of the system to form a multitude of different products ranging from simple compounds such as water and carbon oxides, to various complex carbon compounds such as fullerenes and carbon nanotubes, which may partly be attributed to theoretical and/or experimental shortcomings arising from lack of understanding of the complex free radical mechanism that governs the hydrocarbon conversion, and its interactions with a number of important process parameters. In addition to that, more significantly: the scientific and technical challenges of its activation; owing to factors such as the negligibly small electron affinities, the huge HOMO/LUMO gaps, the perfect-symmetry or poor co-ordinative ability, as well as the incredibly large kinetic-barrier to cleave the C–H bond *at* 438 kJ/mol. Thus, it is the most-stable (least-reactive) of all hydrocarbon molecules [11].

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On top of that, the hazardous-characteristic of the required reactant-mixtures creates enormous engineering challenges that impedes the technological process. It is, however, mention-worthy that methane is, perhaps, the most-attractive substrate, its direct-oxidation to a more energy-dense liquid derivative such as C_1-oxygenate, is still largely-lacking, and till date, does not exist as an industrial technology.

By the middle of the last-century, the partial oxidation of methane, and later on, propane, butane, and mixtures thereof extracted from oil-associated, crude stabilization, and processing gases became a widespread petrochemical process in the United States [12]. The subsequent decline of this technology in the late 1950's was due to the rapid progress of competing technologies based on: (i) pre-conversion of hydrocarbons into syn-gas, and subsequent catalytic synthesis of target products; (ii) development of market for propane and butane as domestic fuel and raw-material for many petrochemical processes; and (iii) difficulty of extracting individual components from a complex mixture of products of the non-selective gas-phase oxidation of C_3– C_4 hydrocarbons, which were used in the then technologies; (iv) small scope of fundamental research, and the lack of clear understanding of the process-mechanism i.e. the partial oxidation technology then, was based solely on empirical knowledge, hence pose a serious obstacle to the improvement of the process.

Although least explored in chemical synthesis, a cleaner and more energetically-efficient method for the conversion of hydrocarbon gases into methanol is photo-chemistry because the key reagent is light of particular energy and also with a tremendous potential to make thermodynamically-difficult reactions proceed at lower temperature, has been considered as an attractive option by research groups [13], [14], and [15]. The application of photo-chemistry, however, is limited by concerns about scalability, efficiency, and safe operations of the processes.

Most activation of alkanes using low-temperature routes are based on transition-metal catalysts such as platinum complexes, and while these system achieve the desired-results under mild-conditions, quite-frankly, they are far-removed from possible future-application on a large-scale process due to expensive-catalysts, and the nature of the obtained-products [11].

While earlier work on the detailed theoretical investigation of the oxidation of methane to methanol under ultra-violet radiation at a wavelength region ($\lambda = 230$ nm) has been reported in literature [15]. As far as I can tell, an in-depth investigation on the conversion of C_3–C_4 fraction into methanol under visible-light excitation ($\lambda = 420$ nm) has not been previously reported anywhere in the literature, hence, this is deemed to be investigation-worthy. The aims of this work are to: (i) formulate the theoretical concept of the processes; (ii) carry out the experimental-procedure; and (iii) perform the quantum-chemical modeling and calculations for the processes. In this present study, it is reported that, methanol formation with a 90 % selectivity can be achieved at a single-pass propane-butane conversion level of 10 % by the influence of nitric-acid solution, at $T = 100^0$C, and P = 1 *atm.*, in a photo-chemical reactor.

Nevertheless, it is note-worthy that during the petroleum refining process, a substantial amount of C_3–C_4 fraction (*existing as a gas-fraction rather than individual component*), is recovered from primary crude oil distillation and also by hydrocarbon cracking of heavy molecules; bulk of which is flared into the atmosphere through the refinery-furnace. Thereby, since economically-viable methanol production from natural and associated gases is the primary concern, further improvements in methanol selectivity and yield have emerged as key issues. On that ground; owing to the higher chemical-reactivities of propane and butane molecules in comparison to methane, the use of C_3–C_4 fraction as an alternative feed-stock for methanol production is, to a great extent, an important aspect of chemical technology and economics.

Theoretical Concept and Mechanism of the Process

Concentrated nitric-acid decomposes according to [Eq. (4)]

already at room-temperature [16]:

$$4HNO_3 \leftrightarrow 4^{\bullet}NO_2 + 2H_2O + O_2 \qquad (4)$$

From a number of extensive studies devoted to alkane oxidation by hydroxyl radical, it has been demonstrated that hydroxyl ($^{\bullet}$OH) radical plays a key reactive intermediate role in combustion chemistry from the groups in [17], [18], and [19], as well as in tropospheric free-radical chemistry as reported from the groups in [20], [21] and [22].

Typically, the photolysis of water molecules ($H_2O + hc/\lambda$ ($\lambda = 180$ nm) $\rightarrow OH^{\bullet} + H^{\bullet}$) is an important source of hydroxyl radical (OH) in the upper atmosphere [23]. The weak longest wavelength tail of water photolysis ($\lambda = 188$ nm) includes the singlet-triplet $X^1A_1 \rightarrow A^3B_1$ transition and the more intense absorption ($\lambda < 186$ nm) is determined by the spin-allowed $X^1A_1 \rightarrow A^1B_1$ excitation of the $n \rightarrow \sigma^*$ type, where σ^* is an anti-bonding water molecular orbital (MO) which easily transforms to the single O-H anti-bonding MO along the photo-dissociation path. However, the energy threshold for photo-chemical decay of water vapor into hydroxyl radical and hydrogen atom [Eq. (6c)] is an uphill process, which requires ~ 235 kJ energy or photons of energy of about ≤ 6.7 eV corresponds to a hard UV region, and therefore an inefficient-source of $OH^{\bullet}$ generation [23 – 24]. In addition, the photo-generated hydroxyl radical initiates a variety of complex side reactions and the electron-donating behavior of the product molecules limits the yield and selectivity of desired product, hence $^{\bullet}$OH radical via water photolysis is non-selective. Hence, such phenomenal nature of $OH^{\bullet}$ radical generation in the low troposphere is impossible since the UV radiation is absorbed by *Schumann-Runge* system of O_2 and by ozone.[24] The photolysis of water can be sensitized through light absorption by NO_2 in [Eq. (5)], and the subsequent photo-chemical reaction of the excited NO_2^* molecule with water [Eq. (6a)] as claimed in [25] and [26].

$$NO_2 + hc/\lambda\ (\lambda = 420 \text{ nm}) \rightarrow {}^{\bullet}NO_2^* \qquad (5)$$

In order to photo-dissociate a molecule, it must be excited above its dissociation-energy (D_0). In the lower troposphere, only molecules with D_0 corresponding to a wavelength $\lambda >$ 290 nm are photo-chemically active. In addition, the molecule should have bright electronic-transitions above D_0. HNO_3, for instance, possesses a low dissociation-energy ($D_0 = 2.15$ eV or 576.6 nm) but, however, requires ultraviolet-excitation for its photolysis because it lacks the appropriate electronic-transitions in the visible region. It is noteworthy that NO_2 dissociation to NO + O (^{3}P) did not occur at this wavelengths from the experimental observation of both [26] and [27]. Formation of OH product in [Eq. (6)] has been confirmed by its characteristic laser induced fluorescence (LIF) [25]. In [25] have recently successfully shown that the reaction of electronically-excited NO_2 with water can be an important source of troposphere-hydroxyl radicals.

$NO_2^{*} + H_2O \rightarrow {}^{\bullet}OH + HONO$ (6a)

$HNO_3 + hc/\lambda\ (\lambda < 335\ nm) \rightarrow {}^{\bullet}OH + {}^{\bullet}NO_2$ (6b)

$H_2O + hc/\lambda\ (\lambda = 180\ nm) \rightarrow {}^{\bullet}OH + H^{\bullet}$ (6c)

The proposed method is based on the principle of activation of alkane-group with a hydroxyl radical obtained from the reaction of water molecule with photo-excited nitrogen dioxide ${}^{\bullet}NO_2^{*}$ [Eq. (6a)].

Upon the interaction of the photo-generated hydroxyl radical with alkane-molecule, hydroxyl-radical reaction proceeds via hydrogen atom abstraction from the C–H bond to form alkyl-radical and water molecule [Eq. (7)]:

$C_nH_{2n+2} + {}^{\bullet}OH \rightarrow {}^{\bullet}C_nH_{2n+1} + H_2O\ \ (n = 3, 4)$ (7)

$C_3H_8 + OH \rightarrow {}^{\bullet}C_3H_7 + H_2O$ (7a)

$C_4H_{10} + OH \rightarrow {}^{\bullet}C_4H_9 + H_2O$ (7b)

Whereas, the subsequent homolytic-decomposition of C–C alkyl radical to form methyl radical and alkene molecule ($C_{n-1}H_{2n-2}$) [Eq. 8] is a well-known radical-chain process in thermal cracking wherein, the selectivity to ${}^{\bullet}CH_3$ is approximately 100 % [15].

$C_nH_{2n+1} \rightarrow {}^{\bullet}CH_3 + C_{n-1}H_{2n-2}\ \ (n = 3, 4)$ (8)

${}^{\bullet}C_3H_7 \rightarrow {}^{\bullet}CH_3 + C_2H_4$ (8a)

${}^{\bullet}C_4H_9 \rightarrow {}^{\bullet}CH_3 + C_3H_6$ (8b)

Under the condition of visible-light radiation of atmospheric oxygen, singlet-state oxygen (${}^1\Delta_g$) may be generated as shown in [Eq. (9)]:

$O_2\ ({}^3\Sigma_g) + h\nu\ (\lambda = 420\ nm) \rightarrow O_2^{*}\ ({}^1\Delta_g)$ (9)

the following process [Eq. (10)] is also possible:

${}^{\bullet}C_nH_{2n+1} + O_2^{*}\,({}^1\Delta_g) \rightarrow {}^{\bullet}C_nH_{2n-1} + {}^{\bullet}OOH\ \ (n = 3, 4)$ (10)

${}^{\bullet}C_3H_7 + O_2^{*}\,({}^1\Delta_g) \rightarrow {}^{\bullet}C_3H_6 + {}^{\bullet}OOH$ (10a)

${}^{\bullet}C_4H_9 + O_2^{*}\,({}^1\Delta_g) \rightarrow {}^{\bullet}C_4H_8 + {}^{\bullet}OOH$ (10b)

Preliminary attempt to nitrate methane in the laboratory was unsuccessful due to the formation of nitro-methane because the **e**xposure time was too short for the reaction temperature [28].

$CH_4 + HNO_3 \rightarrow CH_3NO_2 + H_2O$ (11)

The fact that no reaction between NO_x and alkanes occurs in the absence of O_2 indicates that the presence of both the reagents is a necessary pre-requisite, with NO_2 apparently acting as an initiator of the oxidation. Nonetheless, gas-phase nitration of alkane primarily at low pressures was further developed for the conversion of CH_4-O_2-NO_x to C_1-oxygenates by the groups in [29] and [30]. In these works, it was demonstrated that: (i) when NO or NO_2 was introduced into methane-oxygen system as initiator, methane was able to be oxidized to methanol and formaldehyde, even under ambient pressure; (ii) nitrogen atom in NO_x showed higher activity for cleavage of the C–H bond than oxygen atom, so as to initiate methane oxidation at ambient condition; (iii) introduction of NO_x not only lowers the reaction onset-temperature, but also, dramatically alters the composition of the resulting products. In addition to that, a sharp reduction in the effective activation energy upon NO_x addition was observed. It was, therefore, concluded that gas-phase nitration of alkane at low-temperature favors the selectivity of the reaction to methanol, and that under mild conditions, nitro-methane appears to be an unstable intermediate product.

From in-situ spectroscopic studies of reaction products for the thermal conversion of methane in the gas-phase, neither nitro-methane (CH_3NO_2) nor alkyl nitrite (CH_3ONO) were detected [30]. On that ground, it was therefore amplified by the groups in [31] and later by same [32] that nitro-methane and alkyl nitrate are intermediates and pre-cursors during the partial oxidation of methane. Further, the partial oxidation of methane with nitric-acid vapor (considered as an ${}^{\bullet}NO_2$ source) was investigated [32] and it was suggested that ${}^{\bullet}NO_2$ plays a significant catalytic role in the process, due to the efficient photo-dissociation of nitro-methane and the regeneration of nitrogen-dioxide [33].

${}^{\bullet}CH_3 + H_2O + {}^{\bullet}NO_2 \rightarrow CH_3NO_2 + H_2O$ (12)

Absorption spectrum of nitro-methane in the gas-phase under visible-light excitation ($\lambda = 420\ nm$), and the primary photolytic process following excitation of either of the two lowest optical transitions is characterized by cleavage of the C–N bond to yield methyl radical and nitrogen dioxide as implied by the groups in [34], [35] and [36]˙ The excitation of nitro-methane in the $n - \pi^{*}$ transition is shown in [Eq. (13)].

$CH_3NO_2 + h\nu \rightarrow {}^{\bullet}CH_3 + {}^{\bullet}NO_2$ (13)

${}^{\bullet}NO_2 + H_2O \rightarrow {}^{\bullet}NO_2 - H_2O$ (14)

${}^{\bullet}CH_3 + {}^{\bullet}OH \rightarrow CH_3OH$ (15)

${}^{\bullet}CH_3 + H_2O + {}^{\bullet}NO_2 \rightarrow CH_3OH + HNO_2$ (16)

Above room-temperature, nitrous-acid is unstable, and thus decay into nitrogen-dioxide, nitrogen monoxide, and water molecule [Eq. (17)]. The decomposition product NO is quickly oxidized to NO_2 by molecular-oxygen in [Eq. (18)] even under normal condition, which can be returned to the oxidation cycle, hence, [Eq. (19)] shows that the oxidation of nitrous acid into nitric acid completes a cycle for the catalytic conversion of C_3–C_4 fraction to methanol.

$2HNO_2 \rightarrow NO_2 + NO + H_2O$ (17)

$2NO + O_2 \rightarrow 2NO_2$ (18)

$HNO_2 + ½O_2 \rightarrow HNO_3$ (19)

$(C_3H_8 + C_4H_{10}) + O_2 \rightarrow (H_2O;\ h\nu/HNO_3) \rightarrow 2CH_3OH + (C_2H_4 + C_3H_6)$ (20)

Materials and Methods

Materials

All chemicals used for the experiments were acquired from commercial sources at analytical grade and used without further purification. The propane-butane fraction (C_3–C_4, 99.5 %), and oxygen (99.5 % O_2) were acquired from *Naftogas, Kiev*; 50 μL of 56 % concentratiion of HNO_3 solution (*Azot, Severodonetsk*); and Distilled water (1 dm^3 of H_2O) supplied by *Himrezerv*, *Kiev*.

Experimental Set-up

The oxidative-conversion of propane-butane gas fraction (C_3–C_4) into methanol at a low reaction-temperature (T = 100^0C), an atmospheric-pressure (P = 1 *atm.*), under the influence of nitric-acid vapor, as well as under visible-light irradiation at a wavelength region (λ = 420 nm) was investigated at the laboratory-scale using a photo-chemical reaction vessel (**Fig. 1**). Calculation parameters for the reactor were performed using the MAPLE–14 Software Package.

Experimental Method

Before each run, the reactor was purged with N_2 for about 10 *mins* and then de-coked using 15 % CO_2 : 85 % N_2 mixture to ensure that the reactor-walls and the coupon were coke-free. This was accomplished by visually observing the appearance of the coupon through an observation hole in the furnace and by monitoring the weight of the coupon during the decoking process. If the appearance of coupon was transparent and non-luminous, and its weight did not decrease with time, the coupon was assumed to be coke-free. The reactor was again purged with N_2 for about 10 *mins*, after which the hydrocarbon reactants and steam were introduced. The primary reason for N_2 purge before-and-after the decoking experiments was to minimize the accumulation of potentially-explosive mixtures in the reactor. The photo-chemical reactor (**Fig. 1**, *fabricated by KPM company*, *Moscow*) consists of a 3 L volume made of quartz KU–1 model, equipped with inlet-and-outlet fittings. Mercury vapor-lamps (7) *manufactured by* "*Saransk Electrical Company*, Russia" were used as irradiation sources. A cylindrical-apparatus filled with ion-exchange resins was used as the water-treatment unit (2). Should water asides from distilled-water for experiment, it is strongly-recommended to be sent to the water-treatment vessel (2) for purification; since any presence of carbonates of calcium and magnesium contained therein may clog the reactor-equipment, and consequently, greatly impede the degree of the hydrocarbons conversion.

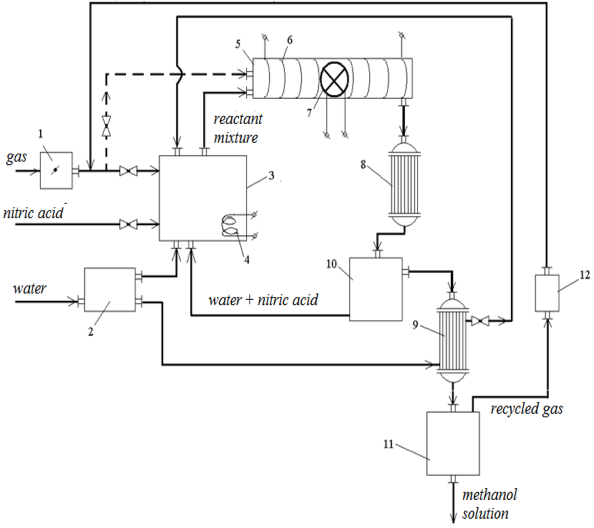


Figure 1. ***Technological Installation of the Reactor*: (1) – Gear; (2) – Water-Treatment Unit; (3)– Hybrid Steam-Boiler; (4)– Electrical-Conductor; (5) – Conversion-Reactor; (6) – Electric-Heater; (7) – Radiation-Source; (8, 9) – Refrigerator; (10, 11) – Condensate-Tank; (11, 12) – Compressor**

The propane-butane (C_3–C_4) fraction, and oxygen were supplied from a pressure-cylinder through a gas-pressure regulation-system at an atmospheric-pressure (P = 1 *atm*.) by the gear (1). The reactant gases consisting of C_3–C_4, and oxygen were mixed with steam, transported through electrically-heated lines (4) into the reactor (5), and subjected to thermal-treatment at low-temperature (T = 100^0C) by the electric-heater (6). The flow-rate desired for the given experiment was varied at (± 5 %). Irradiation of the reaction-mixture was then performed in reactor (5) by using mercury vapor lamp at a wavelength (λ = 420 nm) to prevent high-energy short wavelength radiation from reaching the photo-chemical substrate, and also to enhance greater control over which substrate-chromophores are excited. To calculate the absorbance of a reaction mixture, the transmitted light through pure nitric-acid was used as reference. The boiler gas-steam mixture passes through the main-line, enters into the conversion reactor (5), followed by the condensation of gas-vapor mixture, whereas the initial evaporation process occur after the application of electric-heaters (4) and the heat from gas-combustion. The refrigerators (8, 9) were either air-or-water-filled to cool the gas-vapor mixture to ~ 95^0C in order to ensure the condensation of water and nitric-acid vapors. The condensed water and nitric-acid vapors are separated from the gas-mixture containing methanol in the tanks (10, 11). The tanks (10, 11) are connected to a compressor (12) to ensure continuous-recycling of the unreacted gas-feed.

To ascertain the validity of this hypothesis, three series of experiment were performed.

In the 1st experimental series, the gas–vapor mixture at a ratio = 1: 1 was only fed into the reactor and heated to 100^0C without exposure to irradiation. In the 2nd experimental series, the gas–vapor mixture at a ratio = 1: 1 was fed into the reactor and heated to 100^0C and subsequently exposed to photo-irradiation (λ = 420 nm) via the radiation source. In the 3rd experimental, 50 *м*L of a 56 % conc. of HNO_3 was incorporated into the reaction-mixture at a gas–vapor–acid ratio = 1: 1: 0.1 respectively, and the resulting mixture was fed into the reactor and heated to 100^0C followed by irradiation at 420 nm. The reaction processes depicted by the Equations [5, 6a, 7, 8, 16 – 20] were observed to take place in the reactor during the experimental procedure. The reaction products were cooled to room temperature by circulating water directly through the refrigerators (8, 9) so as to carry out separate condensation-phase in apparatus (10, 11). The resulting products were thereafter separated into their individual components i.e. the liquid reaction products were supplied into the tank (11) while any unreacted gas are recycled. The reaction progress was monitored via an insitu *UV-Visible absorbance spectroscopy*. The gaseous-products were analyzed by using Clarus 500 GC whereas the liquid products were identified using Crystal 2000 M liquid-chromatogram of 3 м long polysorb (*Chromatograph not shown*).

Results and Discussion

At room-temperature, concentrated nitric-acid decomposes into nitrogen-dioxide, oxygen, and water-molecule. Visible absorption of nitrogen dioxide (brown gas) is well-known to be determined mainly by the $X^2A_1 \rightarrow \tilde{A}^2B_2$ ($\sigma\rightarrow\sigma^*$) transition and additionally by the $X^2A_1 \rightarrow B^2B_2$ ($\sigma\rightarrow\pi^*$) excitation. The C^2A_2 state is not accessible by direct photo-excitation of NO_2 from the ground state because the pure electronic $^2A_1 \rightarrow {}^2A_2$ transition is forbidden in electric dipole approximation. With the account of asymmetric stretch b_2 vibrations, such transition becomes vibronically-allowed, thus the $X^2A_1 \rightarrow C^2A_2$ transition of the $\sigma\rightarrow\pi^*$ type also contributes to the visible absorption system of NO_2 [37]. It has been demonstrated by [25] that the photolysis of water can be sensitized through visible-light absorption (λ = 420 nm) by NO_2 and the subsequent photochemical reaction of the excited NO_2^* molecule with water produces hydroxyl radical and nitrous-acid. The experimentally-determined lifetime of NO_2^* at the excitation photon wavelengths region λ = 400 – 490 nm (in the absence of collision) amounts to τ = 40 – 60 μs [38]. Thus, in my point of view, the long lifetime of this state in comparison to the typical collision-time of molecule ($t = 10^{-8}$ s), characterizes nitrogen dioxide O=N–O· (^{2}A") as a reactive meta-stable reagent. to activate water-molecule during collision at a low-pressure and low-temperature.

Upon interaction of the photo-generated hydroxyl-radical with alkane-molecules, the initial attack of alkane-molecules proceeds via a C–H scission (hydrogen-atom abstraction) from alkane molecules by the hydroxyl radical to form water-molecule, and the corresponding alkyl-radicals [Eq. (7a) and (7b)]. Thus, the hydrogen-atom abstraction from alkane fuels larger than ethane (C_2H_6), followed by β-decomposition, leads to the formation of alkyl-radical ($^{\bullet}C_nH_{2n+1}$), which thereafter undergoes uni-molecular dissociation via a mixture of chain-branching and chain-termination reactions. It is, however, mention-worthy that the rate of chain branching strongly depends on the relative rates of hydrogen-atom abstraction from the parent fuel molecule at each hydrogen-atom site.

Alkyl radicals are important intermediates in hydrocarbon combustion, and have received enormous attention from both the theoretical and experimental standpoints by groups in [39], [40], [41], [42] and [43]. The experimental gas-phase studies involving direct interrogation of smaller alkyl-radicals ($\leq C_4$), nevertheless, remain limited to highly-substituted and stable species, or to species detected after trapping by reactive radical scavengers.

Larger alkyl-radicals ($\geq C_4$) are quite very difficult to study experimentally owing to their increasing propensity to undergo isomerization and/or uni-molecular decomposition by various pathways [40]. In addition, sufficient internal-energy is deposited into large alkyl-radicals produced by thermo-chemical methods, hence, inducing multiple secondary reactions that make identification of the primary process difficult. Furthermore, hydrocarbon radicals higher than methyl-radical are thermally-unstable, thus, decompose before being collisionally-stabilized to lower molecular-weight to form methyl-radical (CH_3) and alkene ($C_{n-1}H_{2n-2}$) molecule [Eq. (8)] via C–C β-scission of alkyl radicals. In terms of this process, the selectivity to methyl-radical ($^{\bullet}CH_3$) formation is *approximately* 100 %, which may be attributed to its characteristic longer life-time (τ = 0.02 s) in comparison to alkyl-radicals larger than ethyl-radical ($\tau = 10^{-5}$ s), and because large number of collisions in the expansion minimizes the average internal energy of the radicals in a manner that only energetically-favored decomposition process occur. It is well known that hydroxyl radicals: owing to its high reactivity and though short lifetime ($\tau \approx 10^{-8}$ s), can only react with the reagents in immediate environment of the reaction medium. Moreover, it must not be forgotten that since methyl radical can participate in additional reaction, therefore, [Eq. (15)] completes the reaction-cycle for methanol-synthesis.

Quantum-Chemical Calculations and the Molecular-Modeling Process for Conversion of Propane-Butane Gas to Methanol

The calculation for the reaction energy was made on assumption of primary formation of molecular-adduct (Fig. 2a). With the B3LYP/6-311++G(3*df*,3pd) method, the total energy (E_{total}), zero-point vibrational energy (E_0), and the thermodynamic parameters ($\Delta_rG^0_{298}$, $\Delta_rH^0_{298}$ and $\Delta_rS^0_{298}$) for the reaction between NO_2 ($^2A''$) and H_2O ($^1A_1$), the molecular adduct (Fig. 2a), and the transition state (Fig. 2b) have been calculated in the lowest excited $^2A''$ state for the plane reactive system [Eq. (6a)]. The heat of formation (h_f) for molecular-adduct = – 3.0 kJ/mol , the electronic-energy = – 9.1 kJ/mol, zero-point vibrational-energy E_0 = + 6.1 kJ/mol) is exothermic with low barrier and only requires preliminary photo-excitation to reach the meta-stable $NO_2^*(^2A'')$ state, which needs to survive until collision with water molecule. A weak exothermic-effect of the intermediate complex formation does not strongly influence the heat-balance of the whole reaction, but it's important for preliminary activation of the reactants, their structural transformation and irreversible step-wise transition to the products. The molecular-adduct formation induces some additional deformations in the NO_2^* moiety. The short N=O bond in the complex O=N-O·---H--O-H (Fig. 2a) gets stronger upon complex formation and the N-O$^{\bullet}$ bond becomes weaker and longer, in comparison with the NO_2^* ($^2A''$) molecule. The reaction of water molecule with NO_2 in the ground state cannot occur spontaneously since the change of Gibbs free-energy ($\Delta_rG^0_{298}$) for such process is positive (*+ve*) (*thermodynamically forbidden by spin*). The reaction can occur only in the meta-stable excited $NO_2^*(^2A'')$ state, for which the $\Delta_rG^0_{298}$ value is negative. Moreover, the hydrogen atom transfer step (the most important limiting step) in TS (Fig. 2b) is more close to the beginning of the reaction thus resulting in a relatively low calculated activation-energy (E_a) = + 21.1 kJ/mol.

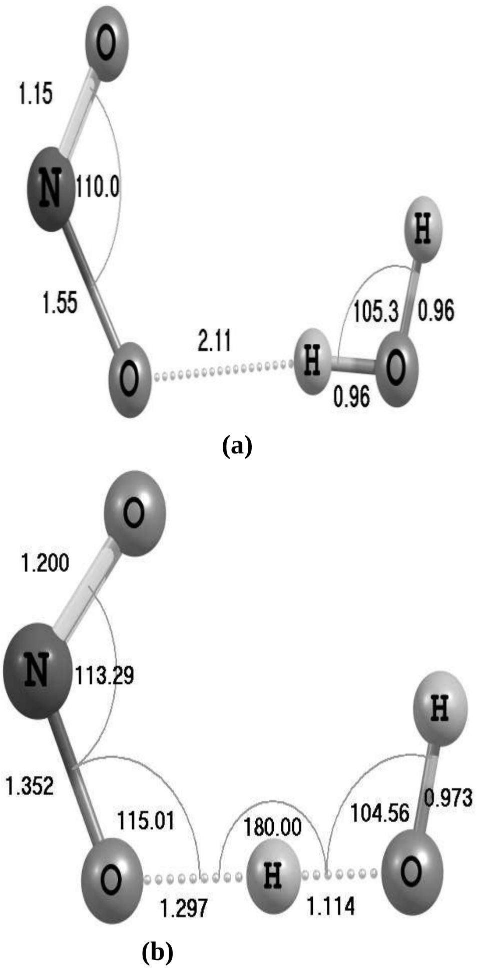


Figure 2. Quantum-chemical DFT B3LYP/6-311++G(3df,3pd) calculations results for optimized structures: (a) Molecular adduct of H_2O and NO_2^*; (b) Transition state (TS) for reaction: $NO_2^* + H_2O \rightarrow HONO + {}^{\bullet}OH$; Bond lengths are in angstroms (Å), Angles are in degrees (°)

Thus, the negative value of Gibbs free-energy $\Delta_rG^0_{298}$ = – 27.8 kJ/mol, and a low E_a value of + 21.1 kJ/mol (**Table 1**) clearly indicate the possibility foe the photo-chemical water decomposition under mild conditions ($\lambda \geq$ 420 nm) in the presence of NO_2. **Fig. 3** illustrates the calculated energy diagram for the excited electronic state NO_2^* ($^2A''$) in relation to the ground electronic state NO_2 ($^2A_1$), and energy profile for the photo-chemical activation reaction: $NO_2^* + H_2O \rightarrow HONO + {}^{\bullet}OH$.

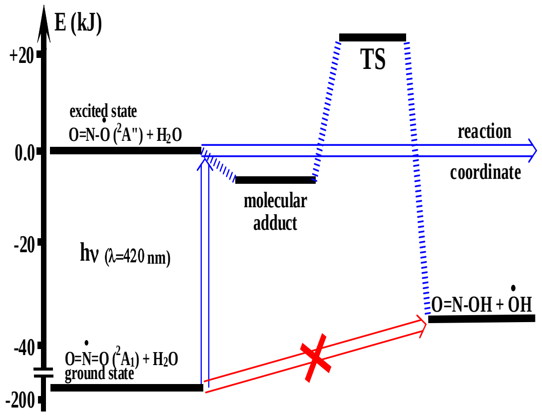


Figure 3. Calculated relative energy diagram for photochemical reaction: $NO_2^* + H_2O \rightarrow HONO + OH$

The structures of the studied hydrocarbon molecules, and their transition states were optimized at the molecular-orbital (MO) level with the possible symmetry constraints control of the 6-311++G(d,p) basis set using the Gaussian-Code. The optimized geometry for propane (**Fig. 4**) and butane (**Fig. 5**) molecules, as well as transition state (TS) structures for the reaction of hydroxylradical and: (*a*) propane molecule (**Fig. 6**); (*b*) butane molecule (**Fig. 7**) are calculated using the Becke's three-parameter hybrid functional and the Lee–Yang–Par exchange correlation functional B3LYP [44, 45] with the help of GAUSSIAN-CODE [46].

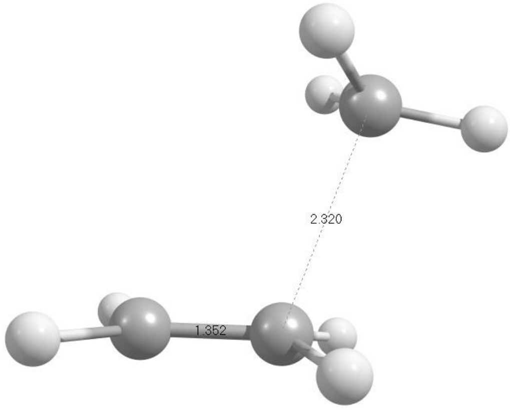


Figure 4. A 3D optimized geometry for C_3H_8 molecule: B3LYP/6-311++G(3*df*,3*pd*) calculation. The equilibrium bond distances are computed in angstrom (Å).

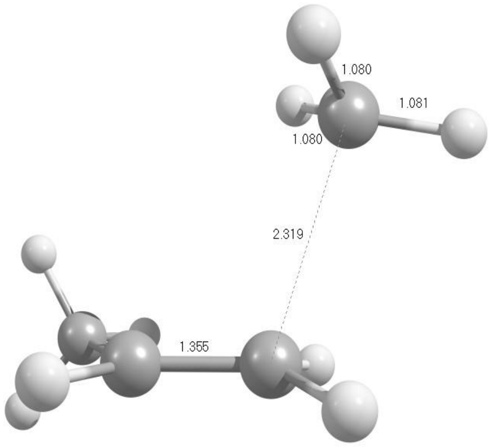


Figure 5. A 3D optimized geometry for C_4H_{10} molecule: B3LYP/6-311++G(3*df*,3*pd*) calculation. The equilibrium bond distances are computed in angstrom (Å)

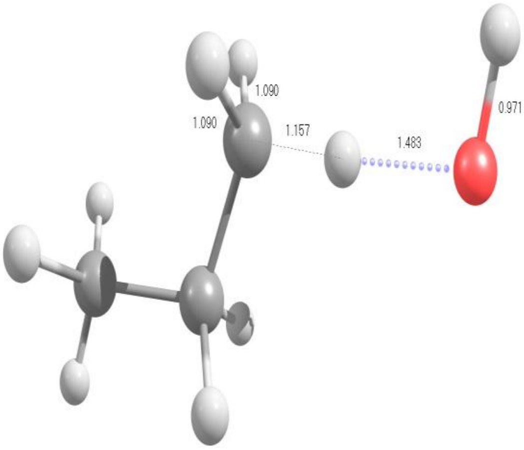


Figure 6. Transition state (TS) structure for the reaction: $C_3H_8 + .OH \rightarrow C_3H_7 + H_2O$, B3LYP/6-311++G(3*df*,3*pd*) calculation. The equilibrium distances in angstroms (Å).

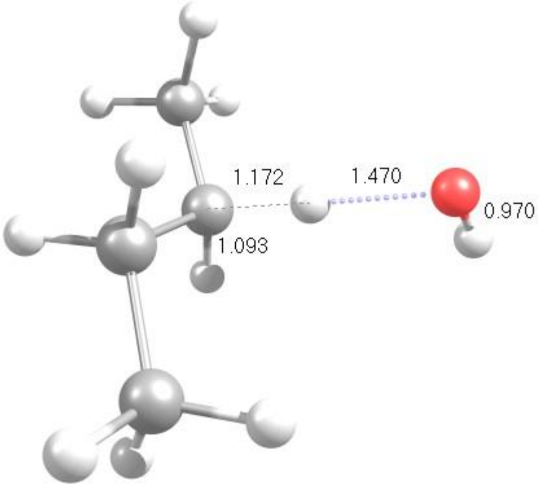
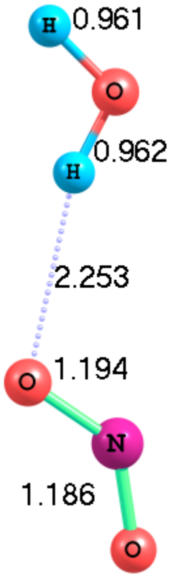
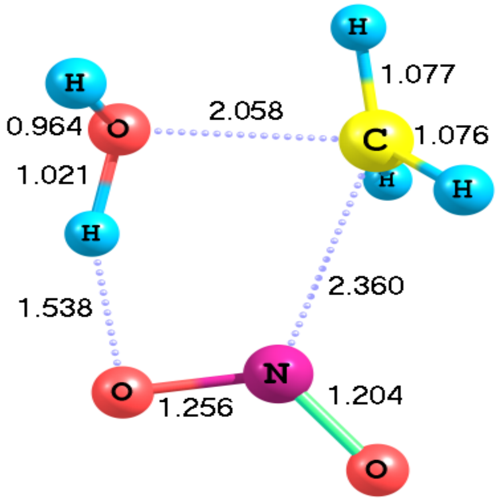


Figure 7. Transition state (TS) structure for the reaction: $C_4H_{10} + {}^{\bullet}OH \rightarrow {}^{\bullet}C_4H_9 + H_2O$, B3LYP/6-311++G(3*df*,3*pd*) calculation. The equilibrium distances in angstroms (Å)



(a)



(b)

Figure 8. Quantum chemical results B3LYP/6-311++G(3*df*,3pd) calculations: (a) Optimized structure of molecular adduct $H_2O–NO_2$; (b) Transition state (TS) for reaction of methyl radical with water molecule (in the presence of NO_2 in ground electronic state). The bond lengths are in angstroms (Å), Angles are in degrees (°)

An optimized transition-state (TS) structure for Eqn. (16) is illustrated above in Fig. 8b. From the optimized transition-state structure (Fig. 8b); upon photo-induced splitting of water-molecule (HOH···ONO bridge in the $H_2O–NO_2$ adduct), it can be seen that nitrogen dioxide abstracts atomic-hydrogen to itself to form nitrous acid (H–ONO); which above room temperature, is unstable, and subsequently undergo decay as shown in Eqn (17). Quantum-chemical B3LYP/6-311++G(3*df*,3pd) calculation results for methanol formation via Eqn. (16) estimates the activation-energy to be intriguingly low (E_a = + 16.4 kJ/mol), and a negative Gibbs free-energy $(\Delta_rG^0_{298})$ value = – 163.3 kJ. For comparison sake's, it is important to state that the reaction of methyl-radical ($.CH_3$) and water-molecule (in the absence of nitrogen-dioxide radical) is characterized by a high activation-energy (E_a) value = + 145.9 kJ/mol. Thereby, it is evident that the rate limiting-step for methanol formation is during the reaction-stage between methyl-radical and water-molecule.

Experimental Result

Effect of all the experimental-conditions on methanol yield: condensate concentration (%) were investigated.

Effect of the Gas-Vapor Ratio on Methanol Yield

The influence of the gas-vapor ratio (varied from 1 to 2) on the yield of methanol was studied but keeping all other reaction parameters to be constant. It can be seen from Fig. 10 that increasing the vapor quantity from 1 to 2 (% mol.) leads to a slight increase in methanol yield, however, the introduction of water-vapor in same amount for the process usually requires an additional-energy. Therebyy, the process is deemed unjustifiable.

Effect of H_2O_2 and HNO_3 Concentration on Methanol Yield

The influence of hydrogen-peroxide (Figure 9) and nitric-acid (Figure 10) concentrations on CH_3OH concentration using mercury vapor lamps DRT–100 at varied vapor-gas ratio were investigated.

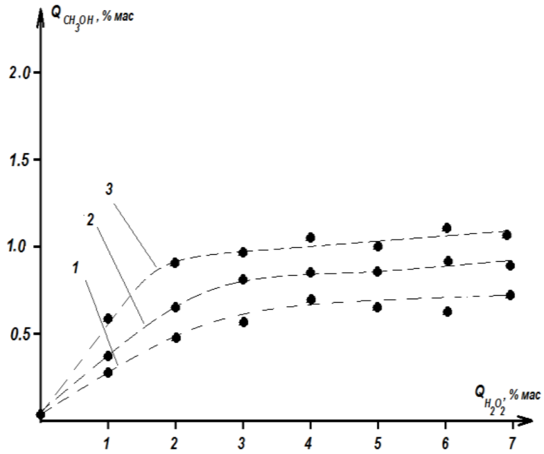


Figure 9. Dependence of CH_3OH yield on the concentration of H_2O_2 (ДRT–100). 1– *vapor-gas* ratio = 1: 2; 2– *vapor-gas* ratio = 1: 1; 3– *vapor-gas* ratio = 2: 1

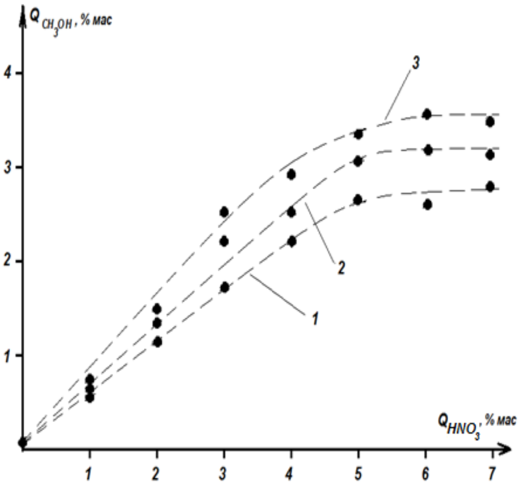


Figure 10. Dependence of methanol yield on the concentration of HNO_3 (ДRT–100). 1– *vapor-gas* ratio = 1: 2; 2– *vapor-gas* ratio = 1: 1; 3– *vapor-gas* ratio = 2: 1

In Fig. 9, it can be seen that the highest methanol-concentration = 1.1 % at an hydrogen-peroxide concentration of 6 %, whereas methanol yield is approximately 1.0 % at an hydrogen-peroxide concentration of 2 %. Upon the introduction of nitric-acid into the vapor-gas system, the maximum methanol concentration of ~ 3.5 % (a 3-*fold* increase) is obtained in comparison to the value of methanol obtained upon hydrogen-peroxide addition. Therefore, it can be concluded that the introduction of hydrogen-peroxide in an amount > 2 % (Fig. 9), practically has no meaningful-effect on methanol yield, as does nitric-acid addition above 6 % concentration (Fig. 10). Further, this indicates that nitric-acid is a more-effective source of hydroxyl radical generation.

Effect of Radiation-Sources on Methanol Yield

The dependence of CH_3OH concentration on different radiation-sources for the $C_nH_{2n+2}–H_2O–HNO_3$ system were investigated using mercury (Fig. 12) and calcium lamps (Fig. 13).

Effect of Mercury-Lamp on Methanol Yield

The dependence of CH_3OH concentration on mercury lamps as the radiation-sources were investigated for the $C_nH_{2n+2}–H_2O–H_2O_2$ (Fig. 11) and the $C_nH_{2n+2}–H_2O–HNO_3$ (Fig. 12) systems.

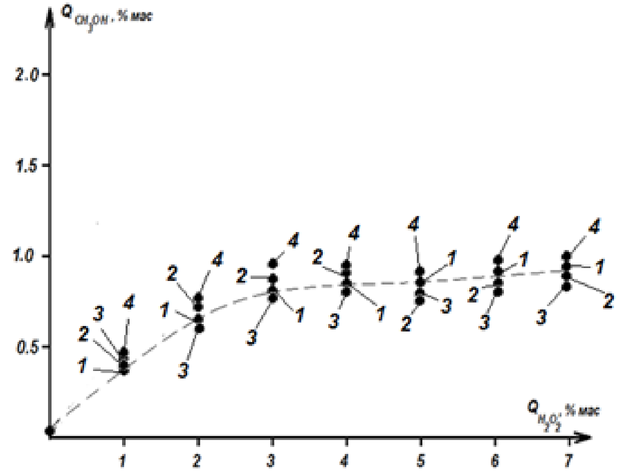


Figure 11. Dependence of CH_3OH yield on the UV radiation source using the C_nH_{2n+2}–H_2O–H_2O_2 system: 1– Mercury-Lamp ДТР–100; 2– Mercury-Lamp ДТР–240; 3– Mercury-Lamp ДТР–400; 4– Mercury-Lamp ДТР–1000.

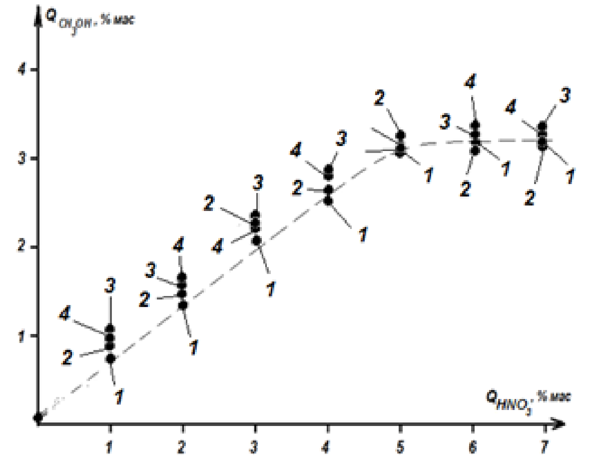


Figure 12. Dependence of CH_3OH yield on the UV radiation source using the C_nH_{2n+2}–H_2O–HNO_3 system. 1– Mercury-Lamp ДТР–100; 2– Mercury-Lamp ДТР–240; 3– Mercury-Lamp ДТР–400; 4– Mercury-Lamp ДТР–1000

In Fig. 12, steady increment in CH_3OH concentration with an increase in nitric-acid concentration are observed. At a 6 % nitric-acid concentration, the highest concentration of CH_3OH = 3.38 %. The spectral-characteristics (*not shown*) and energy-output of the light-source are observed within 410 – 440 nm bandwidth.From the analyses of the experimental results in Fig. 12, it can be concluded that increasing the energy-supply via the radiation source does not lead to a proportional increase in CH_3OH concentration. Additionally, from the results illustrated in Fig. 12, the use of mecrcury vapor-lamp DRT–100 is quite deemed to be sufficent enough for the photo-dissociation of nitric-acid on a laboratory-scale, whereas, owing to the relatively large-size, huge energy-output, and the high reaction-speed of reactant-mixture in the reactor, the lamp DRT–1000 is recommended for industrial-application.

Effect of Calcium-Lamp on Methanol Yield

The dependence of methanol concentration on calcium lamp using different energy-outputs (15 to 40 W) was investigated for the C_nH_{2n+2}–H_2O–HNO_3 system at varied gas-vapor ratio (Fig. 13).

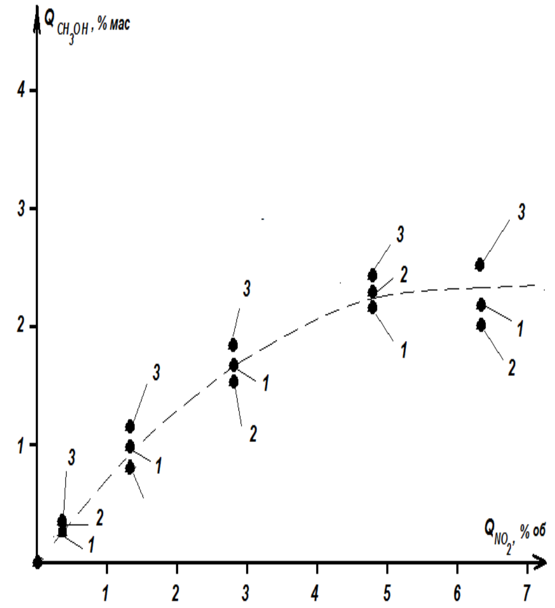


Figure 13. Dependence of CH_3OH concentration on calcium radiation source (λ ~ 420 nм) for the C_nH_{2n+2}–H_2O–HNO_3 system (n = 3,4) at a *vapor-gas* ratio = 1: 1; 1 – 15 W power source; 2 – 20 W power source; 3 – 40 W power source

Without the exposure of reaction-mixture to irradiation, methanol was not formed. From **Fig. 13**, it can be seen that methanol yield increases with an increase in the concentration of NO_2, and that the maximum methanol yield is achieved at a NO_2 concentration of ~ 5 %.

Effect of NO_2 Concentration on Methanol Yield

From the results presented in **Fig. 14**, it can be seen that without the catalytic-influence of NO_2 on the reaction-mixture, the conversion of C_3–C_4 fraction into methanol is not observed. An increase in CH_3OH concentration is observed with an increase in NO_2 concentration, and the maximum CH_3OH concentration is obtained at NO_2 concentration of 5 %.

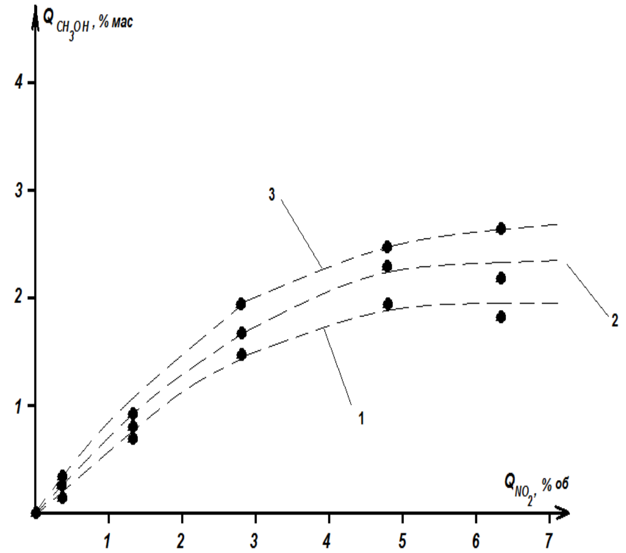


Figure 14. Dependence of CH_3OH yield on the volume-concentration of NO_2 in C_3–C_4 fraction: 1– *vapor-gas* ratio = 1: 2; 2– *vapor-gas* ratio = 1: 1; 3– *vapor-gas* ratio = 2: 1

Table 1. Results of B3LYP/6-311++G(3*df*,3pd) calculations for the total-energy (E_{total}), the zero-point vibration energy (E_0), and the thermodynamic parameters ($\Delta_rG^0_{298}$, $\Delta_rH^0_{298}$ and $\Delta_rS^0_{298}$) for the reaction: $ON\text{-}O^{\bullet} + H_2O\ (^1A_1) \rightarrow ONOH + {}^{\bullet}OH$

Molecular System (electronic state)	B3LYP/6-311++G(3*df*,3*pd*)			Experimental	Values[b]
	Total Energy E_{total}, *a. u.*	E_0^*, kJ/mol [a]	S^0_{298}, J/(mol.K)	S^0_{298},[b] J/(mol.K)	$\Delta_fH^0_{298}$,[b] kJ/mol
$ON\text{-}O^{\bullet}$ ($^2A''$)	– 205.075049	17.2 (0)	254.1	254.1[B]	229.9[B]
+					
H_2O ($^1A_1$)	– 76.4645120	55.9 (0)	188.6	188.8	– 241.8
⇓					
Complex ($^2A''$) **(Fig. 2a)**	– 281.543024	79.2 (0)	372.0	–	–
⇓					
T.S ($^2A''$) **(Fig. 2b)**	– 281.539561 E_a = + 21.1 kJ/mol	68.9 (1) ω = 1905 icm^{-1}	315.3	–	–
⇓					
ONOH ($^1A'$)	– 205.786516	53.1 (0)	248.1	249.4	– 76.7
+					
$^{\bullet}OH$ ($^2\Pi$)	– 75.766245	22.2 (0)	178.2	183.7	+ 38.99
$\Delta_rG^0_{298}$ = – 27.8 kJ	$\Delta_rH^0_{298}$ = – 32.5 kJ [c]		$\Delta_rS^0_{298}$ = – 16.4 J/K	$\Delta_rS^0_{298}$ = – 9.8 J/K	$\Delta_fH^0_{298}$ = – 25.2 kJ

Footnotes

[a] The number of imaginary frequencies in the vibrational spectrum of molecules are given in parenthesis. The absence of imaginary frequencies characterizes the molecular structure as stable (real). The presence of one imaginary frequency (*i*ω) characterizes structure as transition state (TS).

[b] Experimental values of thermodynamic parameters are taken from the National Institute for Standards and Technology (NIST) database:*http://webbook.nist.gov.chemistry*.[69]

[c] Heat of reaction (Δ_rH^0) and the activation energy (E_a) are calculated in the approximation: $\Delta_rH = \Delta_rE_{total} + \Delta_rE_0$. The used relations for energy unit: 1 *a.u.* = 627.544 kcal; 1 *kcal* = 4.184 kJ.

Table 2. Results of quantum-chemical calculations for the total energies (E_{total}), the zero-point vibrational energies (E_0), and the thermodynamic-terms ($\Delta_rG^0_{298}$, $\Delta_fH^0_{298}$, $\Delta_rS^0_{298}$) for the reactants, transition states, and the products of reaction: $C_3H_8 + {}^{\bullet}OH \rightarrow {}^{\bullet}C_3H_7 + H_2O$

Molecular System (electronic state)	B3LYP/6-311++G(3*df*,3*pd*)			Experimental	Values[b]
	Total Energy E_{total}, *a. u.*	E_0^*, kJ/mol [a]	S^0_{298}, J/(mol.K)	S^0_{298},[b] J/(mol.K)	$\Delta_fH^0_{298}$,[b] kJ/mol
C_3H_8 ($^1A_1$) Fig. 4	– 119.1901944	270.3 (0)	268.6	270.0	– 104.70
+					
$^{\bullet}OH$ ($^2\Pi$)	– 75.7662449	22.2 (0)	178.1	183.7	+ 38.99
+					
TS ($^2A_1$) Fig. 6	– 194.9574827 E_a = + 5.2 kJ/mol	290.1 (1) *i*ω = –165 cm^{-1}	370.0	–	–
⇓					
$^{\bullet}C_3H_7$ ($^2A'$)	– 118.5178038	231.0 (0)	304.5	304.9	+ 102.59
+					
H_2O ($^1A_1$)	– 76.4645115	55.9 (0)	188.6	188.8	– 241.80
$\Delta_rG^0_{298}$ = – 87.3 kJ	$\Delta_rH^0_{298}$ = – 73.5 kJ [c]		$\Delta_rS^0_{298}$ = + 46.4 J/K	$\Delta_rS^0_{298}$ = + 40.0 J/K	$\Delta_fH^0_{298}$ = – 75.2 kJ

See footnotes to Table 1

Table 3. Results of quantum-chemical calculations for the total energies (E_{total}), the zero-point vibrational energies (E_0), and the thermodynamic-terms ($\Delta_r G^0_{298}$, $\Delta_f H^0_{298}$, $\Delta_r S^0_{298}$) for the reactants, transition states, and the products of reaction: $C_4H_{10} + {}^{\bullet}OH \rightarrow {}^{\bullet}C_4H_9 + H_2O$

Molecular System (electronic state)	B3LYP/6-311++G(3*df*,3*pd*)			Experimental	Values[b]
	Total Energy E_{total}, *a. u.*	E_0^*, kJ/mol [a]	S^0_{298}, J/(mol.K)	S^0_{298},[b] J/(mol.K)	$\Delta_f H^0_{298}$,[b] kJ/mol
C_4H_{10} (^1A_g) Fig. 5 +	– 158.5174483	345.0 (0)	303.6	310.0	– 125.79
$^{\bullet}OH$ ($^2\Pi$) +	– 75.7662449	22.2 (0)	178.1	183.6	+ 38.99
TS ($^2A_1$) Fig. 7 ⇓	– 234.2875682 E_a = + 6.84 kJ/mol	370.5 (1) $i\omega = -165$ cm^{-1}	365.1	–	–
$^{\bullet}C_4H_9$ ($^2A'$) +	– 157.851544	304.8 (0)	327.8	326.6	+ 72.70
H_2O ($^1A_1$)	– 76.4645115	55.9 (0)	188.6	188.8	– 241.8
$\Delta_r G^0_{298}$ = – 102.54 kJ	$\Delta_r H^0_{298}$ = – 91.35 kJ [c]		$\Delta_r S^0_{298}$ = + 34.8 J/K	$\Delta_r S^0_{298}$ = + 21.8 J/K	$\Delta_f H^0_{298}$ = – 94.33 kJ

See footnotes to Table 1

Table 4. Results of the B3LYP/6-311++G(3*df*,3pd) calculations for the total-energy (E_{total}), the zero-point vibration-energy (E_0), and the thermodynamic-parameters ($\Delta_r G^0_{298}$, $\Delta_r H^0_{298}$ and $\Delta_r S^0_{298}$) for the reaction: $^{\bullet}CH_3 + (H_2O\text{–}NO_2) \rightarrow CH_3OH + HNO_2$

Molecular System (electronic state)	B3LYP/6-311++G(3*df*,3*pd*)			Experimental	Values[b]
	Total Energy E_{total}, *a. u.*	E_0^*, kJ/mol [a]	S^0_{298}, J/(mol.K)	S^0_{298},[b] J/(mol.K)	$\Delta_f H^0_{298}$,[b] kJ/mol
CH_3 ($^2A''_2$) +	– 39.858357	78.0 (0)	194.3	194.2	+ 145.7
$H_2O\text{–}NO_2$ ($^2A'$) **Fig. 8a** ⇓	– 281.62192	83.3 (0)	367.3	428.9*	– 207.6*
TS (^2A) **Fig. 8b** ⇓	– 321.47403 E_a = 16.4 kJ/mol	185.3 (1) $i\omega = 493$ cм$^{-1}$	333.1	–	–
CH_3OH ($^1A'$) +	– 245.109682	130.5 (0)	290.8	279.1	– 81.0
HONO ($^1A'$)	– 76.464512	55.9 (0)	188.6	188.8	– 241.8
$\Delta_r G^0_{298}$ = – 189.2 kJ	$\Delta_f H^0_{298}$ = – 211.5 kJ [c]		$\Delta_r S^0_{298}$ = – 74.8 J/K	$\Delta_r S^0_{298}$ = – 133.8 J/K	$\Delta_f H^0_{298}$ = – 215.8 kJ

An in-situ spectroscopic analysis of the oxidation-products of C_3–C_4 with Crystal 2000 M liquid chromatogram indicates the formation of *methanol*, *ethylene*, and *propylene*. Interestingly, trace amounts of neither oxygenated hydrocarbons e.g. alcohols, aldehydes, ethers, organic acids, and etc), nor volatile nitro-containing compounds such as nitro-methane (CH_3NO_2), alkyl-nitrite (CH_3ONO) in the condensate, were not detected in all the experimental series. It is particularly noteworthy that under the experimental conditions, nitromethane was not detected in the reaction product probably due to: (i) the possibility of its photo-dissociation under the experimental conditions (peak of its absorption spectrum is located at around λ = 300 nm); (ii) the subsequent involvement of $^{\bullet}CH_3$ and $^{\bullet}NO_2$ in the catalytic process of CH_3OH formation; (iii) nitromethane is very labile and, also, characterized by small binding energy ($E_{C\text{–}N}$ = ~ 260 kJ/mol), which is susceptible to cracking in gas-phase oxidation at high temperature (T ~ 800 K). Thereby, the viewpoint that photo-dissociation of nitromethane into $^{\bullet}CH_3$ and $^{\bullet}NO_2$ radicals occurs at low-energy regions ($230 < \lambda < 340$ nм) of the absorption band spectrum, come to terms with the observed experimental-spectra in [35] and [36] and also, is broadly supportive of the suggestions made by [32 – 33] that CH_3NO_2 is an unstable intermediate compound during the gas-phase oxidation of alkane molecules to C_1-oxygenates. In addition to that, the perspective on the catalytic influence of NO_2 on C_3–C_4 oxidation, though complements that of previous literature [15]; however, a 10 % degree of C_3–C_4 conversion (within the target reproducibility limit) was obtained, which significantly exceeds the values of ~ 2.0 % in [33], ~ 3.0 % in [47], and ~ 4.0 % in both the results of [48] and [49**].**

Conclusions

In this study, it is reported that methanol with 90 % selectivity can be achieved at a single-pass C_3–C_4 conversion level of 10 % under the influence of electromagnetic radiation (violet-light) at a wavelength of λ = 420 nm in the presence of water, atmospheric air, and nitric-acid vapor; and under mild reaction conditions at a low-temperature (100^{0}C), atmospheric pressure (1 *atm.*) in a quartz photo-chemical reactor.

The concept and theoretical basis for the direct conversion of propane-butane fraction into methanol is highlighted below [Eq. (1) – (7)]:

$$4HNO_3 \leftrightarrow 4{}^{\bullet}NO_2 + 2H_2O + O_2 \qquad (1)$$

$${}^{\bullet}NO_2 + hc/\lambda\ (\lambda = 420\text{ nm}) \rightarrow {}^{\bullet}NO_2^{*} \qquad (2)$$

$${}^{\bullet}NO_2^{*} + H_2O \rightarrow {}^{\bullet}OH + HONO \qquad (3)$$

$$C_nH_{2n+2} + {}^{\bullet}OH \rightarrow {}^{\bullet}C_nH_{2n+1} + H_2O\ (n = 3, 4) \qquad (4)$$

$$C_3H_8 + OH \rightarrow {}^{\bullet}C_3H_7 + H_2O \qquad (4a)$$

$$C_4H_{10} + OH \rightarrow {}^{\bullet}C_4H_9 + H_2O \qquad (4b)$$

$${}^{\bullet}C_nH_{2n+1} \rightarrow {}^{\bullet}CH_3 + C_{n-1}H_{2n-2}\ (n = 3, 4) \qquad (5)$$

$${}^{\bullet}C_3H_7 \rightarrow {}^{\bullet}CH_3 + C_2H_4 \qquad (5a)$$

$${}^{\bullet}C_4H_9 \rightarrow {}^{\bullet}CH_3 + C_3H_6 \qquad (5b)$$

$${}^{\bullet}CH_3 + H_2O + {}^{\bullet}NO_2 \rightarrow CH_3OH + HNO_2 \qquad (6)$$

$$HNO_2 + \tfrac{1}{2}O_2 \rightarrow HNO_3 \qquad (7)$$

The following important conclusions can be established from this study:

(i) Photolysis of water can be sensitized through light absorption by NO_2 and the subsequent photochemical reaction of the excited NO_2^{*} molecule with water;

(ii) Nitrogen dioxide in the electronically excited state O=N–O· (C^2A'') can play the role of reactive meta-stable reagent if it has a sufficiently long time: $\tau = 40 - 60$ μs;

(iii) The C^2A_2 state at the C_{2v}-symmetry is unstable in respect to the b_2 vibration O-N—O distortion and only this meta-stable NO_2^{*} species is active in reaction (2) with a water vapor;

(iv) With the B3LYP functional, the reaction of electronically excited NO_2^{*} molecule with water vapor to produce ·OH + HONO species, can serve as a source of hydroxyl radicals in the troposphere;

(v) Hydroxyl radical (generated through the hydrolysis of NO_2^{*}) is an effective activator of hydrocarbon molecules;

(vi) Nitrogen-dioxide radical is a highly-efficient acceptor of atomic hydrogen, and can significantly accelerate the limiting-stage of the interaction between alkyl radicals and water molecule during the photo-chemical conversion process of C_3–C_4 fraction to methanol;

(vii) The optimal methanol selectivity (90 %) was achieved by performing the reaction under mild conditions, and in the presence of photo-generated nitrogen (${}^{\bullet}NO_2$) dioxide molecule;

(viii) The oxidative-conversion at a molar ratio of gas–vapor–acid = 2 : 1 : 0.2, T = 100°C, P = 1 *atm*., and under visible-light excitation (λ = 420 *nm*) are optimal conditions for obtaining a high conversion per pass (10 %), % *selectivity* to methanol (90 %).

(ix) The process; in principle, enhances the regeneration of nitric acid, as well as, the formation of low-molecular weight alkenes (*ethylene* and *propylene*: both considered important starting materials in the petrochemical and refining industries);

(x) The broad consistency between the quantum chemical calculation results using the *density functional theory* approach, and experimental investigations has substantiated the mechanism for methanol-formation via the interaction of methyl radical, water, and nitrogen dioxide.

Thereby, this proposed methodology which is similar to that reported in literature [15], and initiated with a recently developed technology [50] for nitric-acid regeneration is considered to be energy-efficient, cost-effective, environmentally-benign, and can serve as a useful guidance to design an industrial plan for the large-scale conversion of propane-butane fraction into methanol.

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