

Article

Formation of Combustible Hydrocarbons and H₂ during Photocatalytic Decomposition of Various Organic Compounds under Aerated and Deaerated Conditions

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Abstract: A possibility of photocatalytic production of useful aliphatic hydrocarbons and H₂ from various organic compounds, including acetic acid, methanol, ethanol and glucose, over Fe-modified TiO₂ is discussed. In particular, the influence of the reaction atmosphere (N₂, air) was investigated. Different gases were identified in the headspace volume of the reactor depending on the substrate. In general, the evolution of the gases was more effective in air compared to a N₂ atmosphere. In the presence of air, the gaseous phase contained CO₂, CH₄ and H₂, regardless of the substrate used. Moreover, formation of C₂H₆ and C₃H₈ in the case of acetic acid and C₂H₆ in the case of ethanol was observed. In case of acetic acid and methanol an increase in H₂ evolution under aerated conditions was observed. It was concluded that the photocatalytic decomposition of organic compounds with simultaneous generation of combustible hydrocarbons and hydrogen could be a promising method of “green energy” production.

Keywords: photocatalysis; hydrocarbons; hydrogen; organic substrates; Fe/TiO₂

1. Introduction

Over the past thirty years increased concerns over emissions of greenhouse gases and the depletion of non-renewable resources of fossil fuels has caused the necessity to look for new methods of energy production. From both the ecological and economical point of view conversion of waste and wastewaters into energy is especially desirable. One of the most promising and popular approaches is biogas generation [1,2]. Biogas is a mixture of different gases, mainly methane and carbon dioxide. Its production during anaerobic digestion involves microorganisms, which results in some serious drawbacks of this technology, as the bacteria responsible for methane generation are very sensitive to the environmental conditions, such as oxygen content, pH or presence of certain organic and inorganic compounds [3]. Therefore, wastes or wastewaters containing substances which are toxic or recalcitrant to these microorganisms cannot be used in the traditional biogas production process.

Application of the photocatalytic process instead of the biological one could remove that restriction. Photocatalysis is not selective for any kind of substrates, therefore it might be used for treatment of all contaminants, even those which are toxic to the methanogenic bacteria [4].

Due to its significant activity, stability and low cost TiO_2 is widely used as a photocatalyst. Most investigations concerning the photocatalytic treatment of organic compounds in aqueous solutions are focused on their complete mineralization to CO_2 and H_2O . Usually, during these experiments the composition of the aqueous phase is only monitored. However, determination of the gas phase composition should be also of interest. There are some reports [5–11] showing that the process of a photocatalytic reduction of CO_2 may lead to methane formation.

The first papers concerning the photocatalytic generation of hydrocarbons from organics in liquid phase were published in the 1970s by Kraeutler and Bard [12–14]. These authors described a photocatalytic decarboxylation of acetic acid under UV light in the presence of Pt/ TiO_2 photocatalyst. The reaction in which CH_4 and CO_2 were evolved as the products was named the “photo-Kolbe” reaction. A few years later Sakata *et al.* [15] reported methane and ethane formation during photodecomposition of acetic and propionic acids in the presence of bare and Pt modified TiO_2 .

A possibility of hydrocarbon formation during photodegradation of C_1 – C_3 alcohols in aqueous suspensions of TiO_2 was investigated by Dey and Pushpa [16]. They concluded that CH_4 and CO_2 were the main products of the reaction of methanol, ethanol and 2-propanol. Other hydrocarbons such as ethane, ethene and propene were also detected; however, at relatively low yields. Similar investigations were conducted by Bahruji *et al.* [17]. The authors used Pt-modified TiO_2 in order to increase H_2 formation. CH_4 , CO_2 , C_2H_6 and C_3H_8 were also identified in the gas phase.

Xu *et al.* [18] reported biomass reforming on Pt/ TiO_2 (anatase-rutile structure) leading to H_2 generation. Methanol, propanetriol, formic acid and glucose were used as the model compounds and sacrificial agents. The possibility of hydrogen production from glucose, sucrose and starch over noble metal-loaded TiO_2 photocatalysts was also described by Fu *et al.* [19]. The results revealed an enhancement of H_2 production in case of Pd and Pt modified TiO_2 and an inhibition of the efficiency in aerated systems.

Recently, Klauson *et al.* [20] described the application of TiO_2 modified with Pt, Co, W, Cu or Fe for the production of hydrogen, oxygen and low molecular weight hydrocarbons from aqueous solutions of humic substances under anoxic conditions. In the presence of all the above materials the

formation of CH₄ was observed, although the highest yield was found in case of Pt-TiO₂. That photocatalyst was also the most efficient when formation of C₂H₄, C₂H₆ and H₂ was taken into account.

In the present work an Fe-modified TiO₂ photocatalyst was applied for the photocatalytic generation of useful hydrocarbons and hydrogen which could be regarded as the potential source of “green energy”. Different organics representing biomass-derived compounds, including an aliphatic acid (acetic acid), aliphatic alcohols (methanol and ethanol) and glucose were used in the experiments. In particular the influence of the reaction atmosphere on the products evolution was investigated. The Fe/TiO₂ photocatalyst was chosen on a basis of our previous investigations [21] during which we found that it exhibits high activity in the “photo-Kolbe” reaction using acetic acid as a substrate.

2. Results and Discussion

2.1. Photocatalytic Decomposition of Various Organic Compounds: The Influence of a Substrate on the Formation of the Gaseous and Liquid Products

Depending on the substrate, different gases were identified in the headspace volume of the reactor (Table 1). In case of acetic acid, the main products of its decomposition were CH₄ and CO₂. Low amounts of C₂H₆, C₃H₈ and H₂ were also identified. During the photocatalytic degradation of alcohols the following gaseous products were identified: CO₂, CH₄ and H₂ in case of CH₃OH and CO₂, CH₄, C₂H₆ and H₂ in case of C₂H₅OH. The gaseous products formed during photodegradation of C₆H₁₂O₆ were CH₄, CO₂ and H₂ (Table 1). The diversity of the products generated from the applied substrates resulted from their different photocatalytic decomposition pathways.

Table 1. Products identified in the gas and liquid phases after 27 h of irradiation over Fe/TiO₂.

Substrate	Composition of a Gas Phase	Composition of a Liquid Phase
CH ₃ COOH	CH ₄ , CO ₂ , C ₂ H ₆ , C ₃ H ₈ , H ₂	CH ₃ COOH, CH ₃ OH, C ₂ H ₅ OH, CO(CH ₃) ₂ , CH ₃ CHO, CH ₃ COOCH ₃
CH ₃ OH	CH ₄ ^a , CO ₂ , H ₂	CH ₃ OH, CH ₃ CHO
C ₂ H ₅ OH	CH ₄ , CO ₂ , C ₂ H ₆ , H ₂	C ₂ H ₅ OH, CH ₃ CHO, CH ₃ OH
C ₆ H ₁₂ O ₆	CH ₄ , CO ₂ , H ₂	C ₆ H ₁₂ O ₆ , CH ₃ CHO, C ₂ H ₅ OH, CH ₃ COOCH ₃

^a in air atmosphere only.

Taking into consideration that some by-products of the organics' degradation must have been generated in the liquid phase, the composition of the reaction solution was also examined. The investigations revealed (Table 1) the presence of trace amounts of acetaldehyde (CH₃CHO) in all cases. Furthermore, methanol (CH₃OH) in the case of acetic acid and ethanol decomposition, and ethanol (C₂H₅OH) and methyl acetate (CH₃COOCH₃) in the case of acetic acid and glucose degradation were identified. In addition, small quantities of acetone (CO(CH₃)₂) were detected during the photodecomposition of acetic acid. The amounts of all the products in the liquid phase were very low and no clear dependence of the liquid phase composition on the reaction atmosphere used was found.

2.2. Effect of the Reaction Atmosphere on Gas Phase Composition during the Photodegradation of Various Organic Substrates

The concentrations of gaseous reaction products evolved with time of irradiation were continuously monitored during the experiments. Figures 1–4 present changes of the amounts of CO₂ and CH₄ in the gaseous phase during the processes conducted under either N₂ or air atmospheres. In Figures 5 and 6 a comparison of the amounts of C₂H₆ and H₂ evolved after 27 h of the decomposition of the model compounds is shown.

Figure 1. Evolution of CH₄ and CO₂ in time of irradiation during the photocatalytic degradation of CH₃COOH. Photocatalyst loading: 1g/dm³; CH₃COOH concentration: 1 mol/dm³; solution pH: 2.6; t = 25 °C.

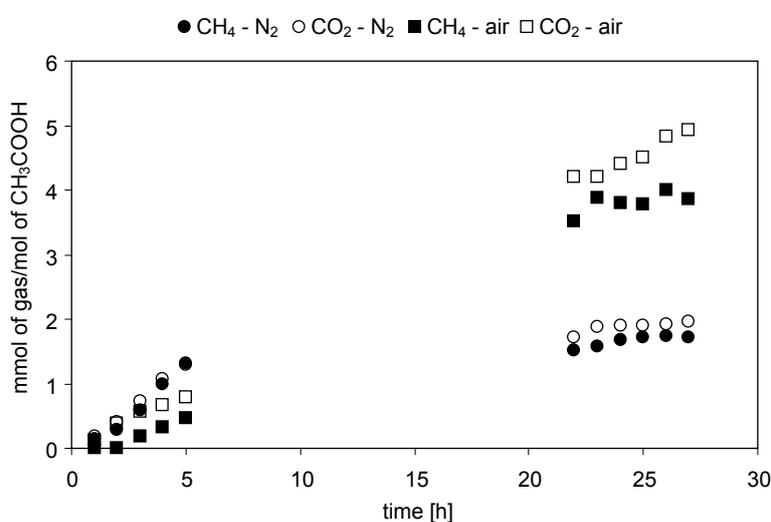


Figure 2. Evolution of CH₄ and CO₂ in time of irradiation during the photocatalytic degradation of CH₃OH. Photocatalyst loading: 1g/dm³; CH₃OH concentration: 1 mol/dm³; solution pH: 6.3; t = 25 °C.

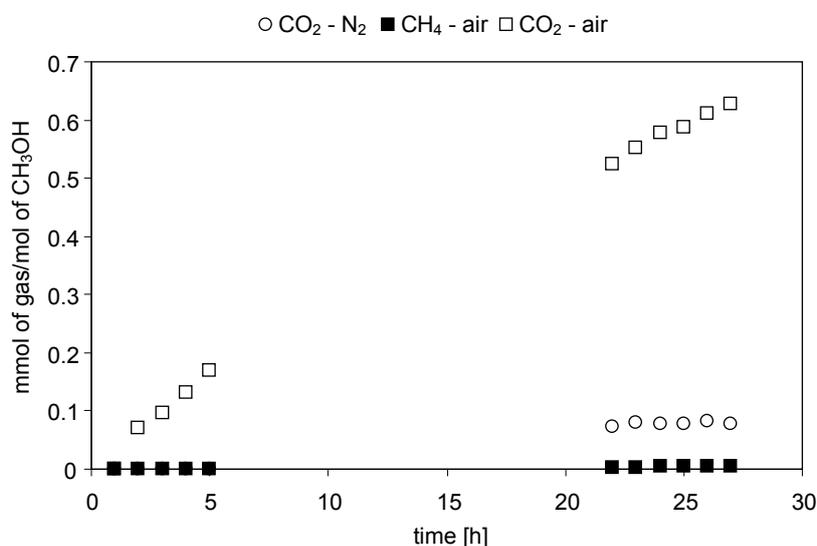


Figure 3. Evolution of CH₄ and CO₂ in time of irradiation during the photocatalytic degradation of C₂H₅OH. Photocatalyst loading: 1 g/dm³; C₂H₅OH concentration: 1 mol/dm³; solution pH: 4.8; t = 25 °C.

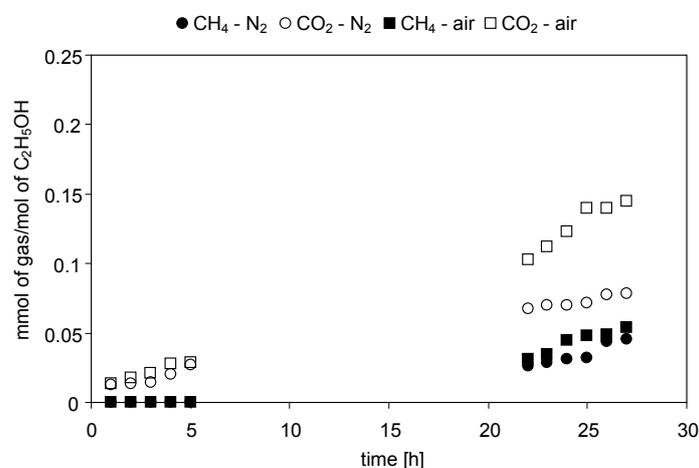
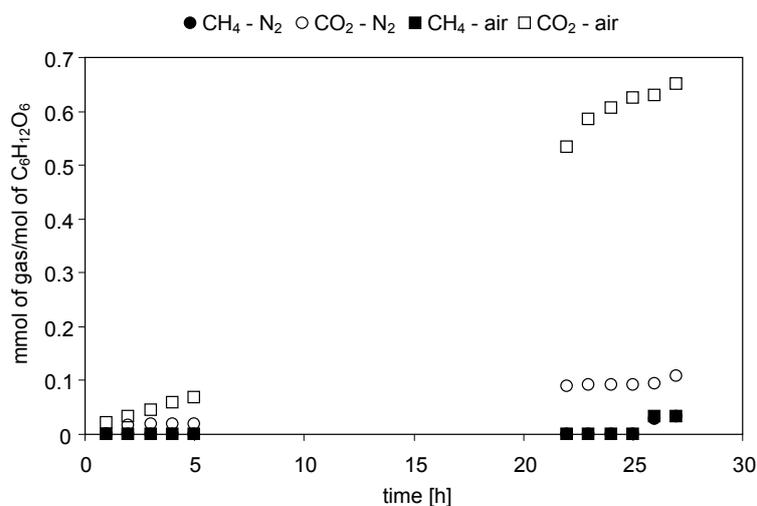


Figure 4. Evolution of CH₄ and CO₂ in time of irradiation during the photocatalytic degradation of C₆H₁₂O₆. Photocatalyst loading: 1 g/dm³; C₆H₁₂O₆ concentration: 1 mol/dm³; solution pH: 5.4; t = 25 °C.

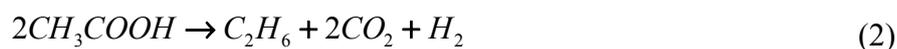


2.2.1. Acetic Acid

In general, the main mechanism responsible for a photocatalytic decomposition of CH₃COOH is its decarboxylation initiated by the photogenerated holes (h⁺). This reaction, known as the “photo-Kolbe” reaction, leads to the production of one mole of CO₂ and one mole of CH₄ from one mole of CH₃COOH:



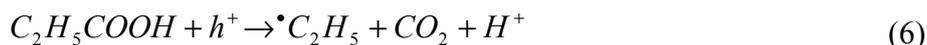
Moreover, recombination of methyl radicals might take place, which results in a formation of C₂H₆, except from CH₄ [12–15,21–24]. Formation of C₂H₆ and H₂ can be written as follows:



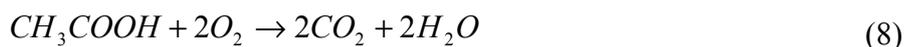
Further, as can be seen in Table 1, formation of C₃H₈ can also occur. A possible mechanism of propane generation can be as follows [15]:



or:



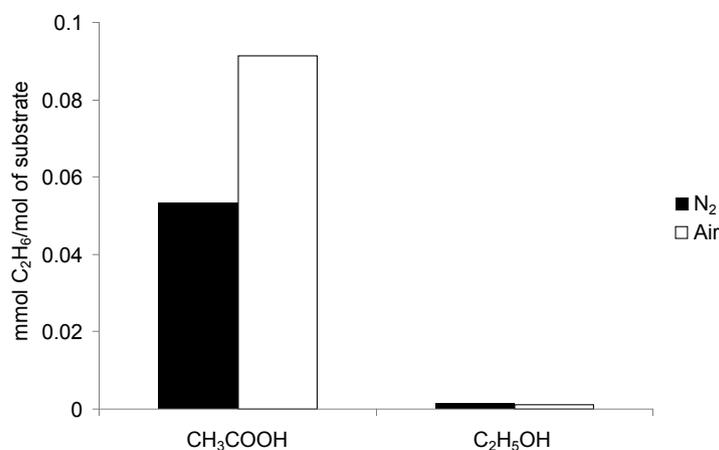
Nevertheless, the present results clearly show that the CH₄/CO₂ ratio after 27 h of irradiation was 0.88 when a N₂ atmosphere was applied and 0.78 when the process was conducted in the presence of air. This suggests that reaction (1) was not the only one proceeding in the system. From Table 1 it can be found that aside from methane, ethane was also formed. In this process methyl radicals are consumed. Therefore, the amount of ethane should be also taken into consideration. Assuming that two methyl radicals form one molecule of C₂H₆ the CH₃[•]/CO₂ ratio can be calculated. After 27 h of irradiation of acetic acid solution the amount of C₂H₆ evolved in a N₂ atmosphere was 0.05 mmol C₂H₆/mol CH₃COOH, whereas under aerated conditions it was 0.09 mmol C₂H₆/mol CH₃COOH. Thus, the CH₃[•]/CO₂ ratio was 0.93 and 0.82 for N₂ and air atmosphere, respectively. However, the values are still below 1. Incorporation of C₃H₈ in the calculations also does not allow one to get a ratio of 1, since the amount of propane was an order of magnitude lower than that of ethane. These results suggest that formation of carbon dioxide might also be due to the mineralization of CH₃COOH to H₂O and CO₂:



Reaction (8) is understandable when the aerated conditions are considered; however, the obtained results revealed that it also proceeded in the N₂-purged system. In our previous paper [21] we have discussed higher evolution rate of CO₂ compared to CH₄ by the reaction of CH₃COOH with the photogenerated oxygen. This O₂ as well as the hydroxyl radicals might be responsible for the mineralization of CH₃COOH [21], which leads to higher CO₂ evolution.

The results shown in Figure 1 revealed that the amounts of CH₄ and CO₂ evolved under aerated conditions were more than two times higher compared to a N₂ atmosphere (1.72 vs. 3.85 mmolCH₄/molCH₃COOH and 1.95 vs. 4.93 mmolCO₂/molCH₃COOH, respectively, after 27 h). Higher efficiency of CH₄ evolution under the aerated conditions can be explained by more effective separation of e⁻/h⁺ pairs in the presence of O₂, being an efficient electron scavenger, and acetic acid, which is known as an effective hole scavenger. Therefore, in the presence of both oxygen and CH₃COOH the “photo-Kolbe reaction” should occur more easily, what was confirmed by the results presented in Figure 1. Moreover, it was found that the concentration of O₂ in the headspace volume of the reactor decreased from 21 to 12 vol.% after 27 h of irradiation, which confirms that oxygen was consumed in the process.

Figure 5. Comparison of the amounts of C₂H₆ evolved during the photocatalytic degradation of various organic substrates after 27 h of irradiation in the presence of Fe/TiO₂. Photocatalyst loading: 1g/dm³; substrate concentration: 1 mol/dm³; t = 25 °C.



The obtained results (Figure 5) also revealed higher efficiency of C₂H₆ evolution in the aerated compared to the N₂ purged system. Ethane formation (Reaction (2)) is initiated by the photogenerated holes, therefore, can easily proceed under both deaerated and aerated conditions. However, like in case of methane, more efficient separation of e⁻/h⁺ pairs contributes to the enhancement of ethane formation. Moreover, the presence of O₂ can result in the increase of the amount of C₂H₆ by enabling of its formation according to the following equation [23,24]:

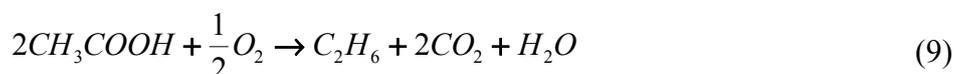
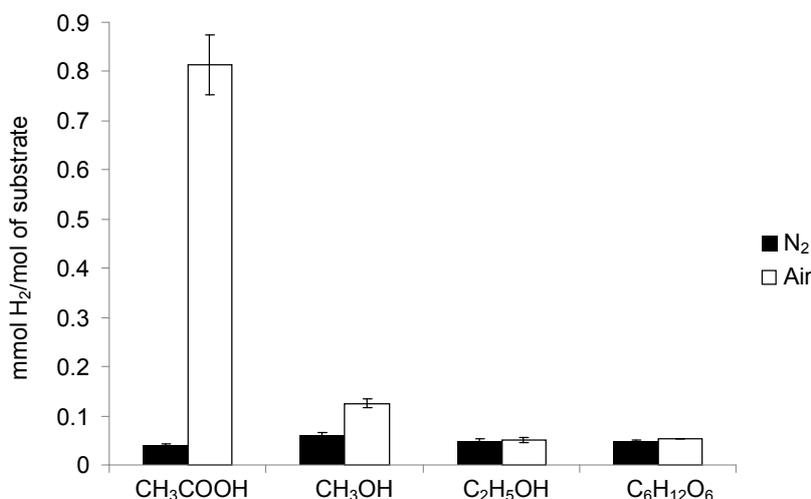


Figure 6. Comparison of the amounts of H₂ evolved during the photocatalytic degradation of various organic substrates after 27 h of irradiation in the presence of Fe/TiO₂. Photocatalyst loading: 1g/dm³; substrate concentration: 1 mol/dm³; t = 25 °C.



As shown in Table 1, amongst the products of CH₃COOH decomposition hydrogen was also present. As in case of other gases, evolution of H₂ was significantly higher in an air atmosphere compared to a N₂ one (Figure 6). After 27 h of irradiation the amounts of H₂ were 0.04 and

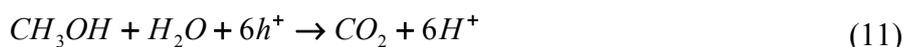
0.81 mmolH₂/mol CH₃COOH in N₂ and air purged system, respectively. The data discussed above show that the photocatalytic conversion of CH₃COOH into hydrocarbons and hydrogen was significantly more effective in the presence of air than in the N₂ purged system.

2.2.2. Methanol

The photocatalytic degradation of methanol under deaerated conditions can be written as [25]:

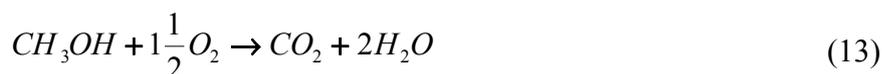


This reaction can also be represented as two half-reactions of oxidation and reduction, respectively:



As reported by Chen *et al.* [25], Reaction (12) cannot occur easily in an aerated system because only few hydrogen atoms are formed in the presence of oxygen. Under such conditions, oxygen is more competitive in capturing the photogenerated electrons, which eventually leads to the formation of H₂O₂ and OH[•].

The obtained results (Table 1) revealed formation of CO₂ and H₂ as the only gaseous products of CH₃OH decomposition in N₂ atmosphere, which confirms the mechanism presented by Equations (10)–(12). Nonetheless, if the only reaction occurring in the investigated system were Reaction (10), the H₂/CO₂ ratio should be equal to 3, but the experimental data show that the ratio is significantly lower (*ca.* 0.7–0.8). This suggests that some other reactions proceeded in the system. As in case of CH₃COOH, such a reaction can be mineralization of CH₃OH yielding CO₂ and H₂O as products [24]:



During the experiments conducted in the air-purged system, the evolution of methane, except from CO₂ and H₂, was observed (Figure 2). Its concentration in the gaseous mixture was, however, very low and after 27 h of irradiation it only amounted to 4.26 μmol/molCH₃OH. Nonetheless, the observed formation of CH₄ might lead to a conclusion that the mechanism of methanol decomposition in the presence of air is not as simple as the one described by Equation (13). For example, a possibility of CO₂ photoreduction cannot be excluded here [16]. Dey and Pushpa reported that carbon dioxide, generated during mineralization of methanol, could undergo a methanation reaction by e[−] and yield CH₄. In the case of greater amounts of CO₂ (as is the case in this work, when the system was aerated) there is a better chance of it being reduced, which can explain the results shown in Figure 2.

The amount of CO₂ evolved in the presence of air was at the end of the experiment about eight times higher compared to the N₂ atmosphere (0.627 vs. 0.078 mmolCO₂/mol CH₃OH, respectively). High CO₂ evolution was an effect of methanol mineralization (Equation (13)) and was accompanied by a decrease of O₂ concentration in the gaseous phase (from 21 to 16 vol.%). It was also observed that in the presence of N₂ no gaseous product evolved from the reaction mixture within the initial 5 h of the experiment. On the contrary, when the reaction was conducted under aerated conditions the evolution of CO₂ started after 2 h of irradiation.

Evolution of hydrogen was significantly lower compared to that of CO₂ (Figure 6). After 27 h of irradiation the amount of H₂ was 0.06 and 0.13 mmolH₂/mol CH₃OH in the N₂ and air purged systems, respectively.

2.2.3. Ethanol

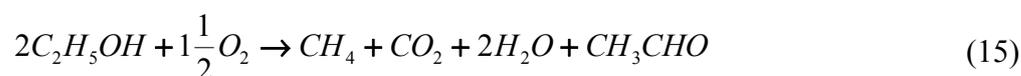
In the case of ethanol, the main products identified in the gaseous mixture were CH₄ and CO₂ (Figure 3). Moreover, some amounts of C₂H₆ and H₂ were also identified (Figures 5 and 6). The CH₄/CO₂ ratio was higher in N₂ than in an air atmosphere and amounted to 0.83 and 0.05, respectively. This resulted from significantly higher CO₂ evolution in the presence of air compared to the N₂-purged system (1.45 vs. 0.078 mmolCO₂/mol C₂H₅OH after 27 h). As in case of other substrates a decrease of O₂ concentration in the gaseous phase in case of the experiments conducted under aerated conditions was found (from 21 to 15 vol.%). It was also observed that the amount of methane obtained under both conditions was comparable (Figure 3).

Decomposition of ethanol is more complex compared to methanol due to the presence of the ethyl group in the C₂H₅OH structure. As a result, the range of intermediate degradation products is very wide [25]. In case of the deaerated conditions the overall reaction of ethanol decomposition can be written as follows [17,24]:



The reduction reaction can be represented by Equation (12), like in case of methanol [25]. However, the oxidation reactions are different. Generally, methane can be produced either by the reaction of free methyl radicals with H[•] or ethanol, or the reaction of acetic radicals with ethanol [24]. In case of the present research, since acetic acid was not identified in the liquid phase (Table 1), the most probable pathway of CH₄ formation was the one involving CH₃[•] and C₂H₅OH. Moreover, as in case of methanol [16], the reduction of CO₂ leading to the methane production cannot be ignored here. Furthermore, methyl radicals can also recombine yielding C₂H₆ as the product (Figure 5).

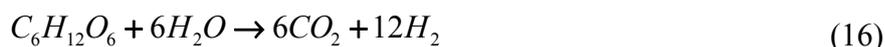
In the presence of oxygen the decomposition of ethanol can be described by the following equation [24]:



Equation (14) indicates that H₂ should be present amongst the ethanol decomposition products. Indeed, the analysis of the gaseous phase composition revealed evolution of hydrogen under both the aerated and deaerated conditions (Figure 6). Furthermore, H₂ could be produced by a degradation of the intermediate products present in the liquid phase (CH₃CHO, CH₃OH, Table 1). However, taking into account that their concentrations were very low, this pathway was of minor importance. The amount of H₂ formed in the N₂ purged system was comparable to that in the aerated system (0.049 vs. 0.051 mmolH₂/molC₂H₅OH, respectively). If we recall the methane evolution under aerated and deaerated conditions (Figure 3) we may find that the reaction atmosphere did not clearly influence the effectiveness of H₂ and CH₄ formation during ethanol decomposition.

2.2.4. Glucose

The photocatalytic reforming of $C_6H_{12}O_6$ is a very complex process which proceeds through numerous steps, in which intermediates such as carboxylic acids, aldehydes and hydrocarbons are formed [19,26]. A detailed probable mechanism of glucose degradation under anaerobic conditions leading to the formation of H_2 and CO_2 was recently discussed by Fu *et al.* [19]. The overall reaction can be written as:



The present research confirmed the formation of CO_2 and H_2 (Figures 4 and 6). In addition, small amounts of CH_4 were identified as well. From Figure 4 it can be found that the amount of CO_2 was higher in the presence of air compared to a N_2 atmosphere, which is consistent with the results observed for other substrates. After 27 h of irradiation the amount of CO_2 in the gaseous mixture was 0.65 mmol CO_2 /mol $C_6H_{12}O_6$ and 0.11 mmol CO_2 /mol $C_6H_{12}O_6$ for air and N_2 , respectively. In the experiment conducted under aerated conditions the concentration of O_2 in the gaseous phase decreased from 21 to 15 vol.% which confirms its consumption during glucose decomposition.

No significant difference between the efficiency of hydrogen evolution in the two systems was observed. In case of the N_2 -purged system the amount of H_2 was 0.048 mmol H_2 /mol $C_6H_{12}O_6$, whereas in case of the aerated system, it was 0.054 mmol H_2 /mol $C_6H_{12}O_6$ (Figure 6). Similarly, no difference in the amount of methane evolved in the presence and in the absence of oxygen was found. After 27 h of the reaction in both N_2 and air atmospheres, the amount of CH_4 reached 0.033 mmol CH_4 /mol $C_6H_{12}O_6$ (Figure 4). The observed evolution of methane can be explained by decomposition of by-products formed in the liquid phase (Table 1) as well as CO_2 photoreduction, as discussed earlier.

2.3. Hydrogen Evolution in the Presence of Oxygen: a Point of Discussion

The results discussed above revealed that the presence of oxygen at a concentration of 21 vol.% or less (*i.e.*, oxygen in air) did not suppress hydrogen evolution during the photodegradation of organic compounds in the performed experiments. What is more, in the cases of acetic acid and methanol a significant enhancement of H_2 formation was even observed (Figure 6). This is somewhat unusual in view of the electron acceptability of O_2 and the competitiveness with H^+ for electron scavenging [16,19,24,25,27].

In order to investigate if the observed phenomenon resulted from the presence of Fe in the photocatalyst structure, an additional experiment was performed. A TiO_2 photocatalyst prepared in a similar way to the Fe/ TiO_2 , but without impregnation with $Fe(NO_3)_3$, was applied in a process of photocatalytic CH_3COOH degradation under N_2 and air atmosphere. After 27 h of irradiation it was found that the effectiveness of evolution of CH_4 and H_2 in the air purged system was higher by 65 and 45%, respectively, compared to the N_2 atmosphere. Therefore, it was concluded that the addition of iron was not responsible for the phenomenon described above.

There are very few papers reporting that O_2 does not affect negatively or could have a positive influence on hydrogen photogeneration [28–30]. Korzhak *et al.* [28] found that when a small amount of air was introduced to a photocatalytic system containing ethanol, the yield of H_2 formation increased. However, in case of mixtures saturated with oxygen or air, hydrogen formation was almost

completely suppressed. The authors contributed the observed increase in hydrogen production to the fact that under such conditions the reactions of O₂ with active free organic radicals take place with high rate constants. Therefore oxygen is consumed mainly in the process leading to the evolution of additional amounts of hydrogen. Moreover, dissolved oxygen might be involved in stabilization of the radical intermediates thus could enhance the reaction efficiency [31]. Furthermore, organic substrates such as acids, alcohols or glucose, contribute to the improvement of charge separation by scavenging of photogenerated holes and consuming O₂ in diverse direct oxidation reactions, which leads to a decrease of the oxygen concentration [32–34].

Anyhow, the majority of the work on hydrogen generation with semiconductors dispersed in a solution is carried out in an oxygen-free atmosphere to avoid the back recombination processes, oxygen interferences with the photocatalyst which occurs while forming of superoxides and/or peroxides and the competition of O₂ and H⁺ for the reduction sites [15,17–19,26,32,35–37]. Most of the papers which describe the photocatalytic degradation of organics in the presence of O₂ are focused on its total mineralization, thus the evolution of H₂ is not discussed. We have proved that the negative O₂ influence on the H₂ generation from different organic substrates is not so evident. In some cases (e.g., decomposition of acetic acid) an increase in H₂ evolution yield can even be obtained. Therefore, a broad and detailed discussion is needed in order to explain the discussed phenomenon.

3. Experimental Section

3.1. Photocatalyst

The photocatalyst used in this study was described in details in our previous paper [21]. In brief, the Fe/TiO₂ was prepared by an impregnation method using crude TiO₂ obtained from the Chemical Factory “Police” (Police, Poland) and (Fe(NO₃)₃) as the Fe precursor. The sample was calcined at 500 °C. The amount of Fe introduced to the sample was 20 wt.%. The Fe/TiO₂ contained anatase, rutile and Fe₂O₃ phases. The crystallite size of anatase and the anatase over rutile ratio were equal to 9 nm and 87:13, respectively. The specific surface area S_{BET} was 82 m²/g.

3.2. Photocatalytic Reaction

The photocatalytic reaction was conducted in a cylindrical quartz reactor (type UV-RS-2, Heraeus, Hanau, Germany) equipped with a medium pressure mercury vapour lamp (TQ-150, λ_{max} = 365 nm). The total volume of the reactor was 765 cm³ (350 cm³ of a liquid phase and 415 cm³ of headspace). In the upper part of the reactor a gas sampling port was mounted. At the beginning of the experiment 0.35 dm³ of CH₃COOH, CH₃OH, C₂H₅OH or C₆H₁₂O₆ solution and 1 g/dm³ of the photocatalyst were introduced into the reactor. The concentration of the organic substrates was 1 mol/dm³ in all the experiments.

Before the photocatalytic reaction N₂ (in order to eliminate the dissolved oxygen) or air were bubbled through the reactor for 1 h. Then, the gas flow was stopped and UV lamp, positioned in the centre of the reactor, was turned on to start the photoreaction. The process was conducted for 27 h. The reaction mixture containing the photocatalyst in suspension was continuously stirred during the experiment by means of a magnetic stirrer. All the experiments were repeated at least twice in order to

confirm the reproducibility of the results. Gaseous products of the reaction were analyzed using a SRI 8610C GC (SRI Instruments, Torrance, CA, USA) equipped with TCD and HID detectors, and Shincarbon (carbon molecular sieve; 2 m, 1 mm, 100–120 mesh), molecular sieve 5 Å (3 m, 2 mm, 80–100 mesh) and 13× (1.8 m, 2 mm, 80–100 mesh) columns. Helium was used as the carrier gas. The composition of the liquid phase was determined using a SRI 8610C GC equipped with a FID detector and a MXT[®]-1301 (60 m) column. Hydrogen was used as the carrier gas.

4. Conclusions

The possibility of photocatalytic generation of combustible hydrocarbons and hydrogen from various organic substrates, including an aliphatic acid (CH₃COOH), alcohols (CH₃OH, C₂H₅OH) and sugar (C₆H₁₂O₆) was demonstrated. The composition of the gaseous phase was influenced by both the applied substrate and the reaction atmosphere. In general, higher efficiency of hydrocarbon and hydrogen generation was obtained under aerated conditions, which is very advantageous from the point of view of possible future applications. In the presence of air, the gaseous phase contained CO₂, CH₄ and H₂, regardless of the substrate used. Moreover, formation of C₂H₆ and C₃H₈ in the case of acetic acid and C₂H₆ in the case of ethanol was observed.

The obtained results revealed that the presence of oxygen did not suppress hydrogen evolution during the photodegradation of organic compounds. In the cases of acetic acid and methanol a significant enhancement of H₂ formation was even observed. Further investigations concerning this issue as well as the improvement of the efficiency of the presented system are in progress.

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Author Contributions

Sylwia Mozia designed the study, managed the literature search and was involved in writing the first draft and data collection. Aleksandra Kułagowska performed measurements and was involved in manuscript writing. Antoni W. Morawski participated in analysis and data interpretation. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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Sample Availability: Samples are not available.

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