Investigation of hydrocarbon oil transformation by gliding arc discharge: comparison of batch and recirculated configurations

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Abstract: The degradation of liquid dodecane was studied in a gliding arc discharge of humid argon or nitrogen. A batch or recycling configuration was used. The products in the gaseous and liquid phase were analysed and for the liquid were found to contain a wide range of hydrocarbons oxygenated species and aromatics. Overall, the study shows promising results for the organic liquid waste treatment, especially in the recycling mode.

Keywords: gliding arc discharge, dodecane, plasma-liquid treatment, hydrocarbon oil

1. Introduction

The transformation of hydrocarbons into benign or reusable species is subject of much activity within the plasma chemistry community. The conversion of gaseous hydrocarbons such as methane and propane into hydrogen and syngas by reforming or into other organic species such as alcohols and acids by oxidative conversion has been studied using a wide range of plasma systems including the combination of plasma with catalyst. Significantly less attention has been paid to larger hydrocarbons which are normally liquid. In this presentation, we use a gliding arc discharge (GAD) in humid nitrogen or argon to examine the plasma chemistry of the transformation of the oil, dodecane, which is an aliphatic hydrocarbon, \( C_{12}H_{26} \). In particular, we look at the effect of the oil being processed as a batch in the GAD reactor or being recirculated [1].

2. Experimental

Low temperature atmospheric plasma was generated using an AC gliding arc discharge reactor as illustrated in Fig. 1 for the batch and recirculated configurations. The effect of different carrier gases (Ar and N₂) on the degradation efficiency and distribution of end-products is investigated using FTIR quantitative and qualitative analysis for the gaseous products and ATR-IR and GC-MS for the liquid phase. The GAD reactor consists of two stainless steel diverging electrodes, 4 mm thick with adjustable width, located under a feeding gas nozzle of i.d. 1.5 mm. An AC neon sign power supply provided a high voltage up to 20 kV p-p at a frequency of 50 Hz. The carrier gases (N₂ and Ar, both 99.998% purity) at a total flow of 5 L min⁻¹ could be humidified by being bubbled through water (H₂O = 2.3 ± 0.3 %). For the batch experiments, 15 ml of dodecane was placed underneath the gliding arc discharge in the plasma-liquid surface treatment. In the recirculated mode, 60 ml of dodecane was pumped (120 ml min⁻¹) from a reservoir beneath the discharge and sprayed into the discharge through a nozzle (1.7 mm) located just below the electrodes.

![Fig. 1. Schematic diagram of the experimental configuration for the plasma-liquid experiments in the batch mode (upper panel) and in the recycled mode (lower panel).](image-url)
intervals of \( t = 5, 20, 30, 40, 50 \) and 60 min. GC-MS analysis was performed on the initial oil samples to quantify the level of by-products formed. In order to facilitate a more detailed analysis, column chromatography was used to collect non-polar and polar fractions which were then subjected to ATR IR and GC-MS liquid analysis.

3. Experimental Results

For the experiments, analysis of end-products in both the liquid- and gas-phases was performed. It was noted that the interaction of the plasma plume with the liquid resulted in evaporation of the dodecane oil. An overall summary of the conversions are given in Table 1 where it can be seen that the increased plasma power in the humid nitrogen plasma increases the rate of evaporation.

Table 1. Summary of results of the GAD plasma-liquid degradation of dodecane using batch and recycling treatment. The Initial volume of dodecane was 15 ml in the batch and 60 ml in the recycling treatment. GC-MS analysis has been performed to quantify the amount of liquid by-products in the samples after treatment.

| GAD gas | Pin / W | oil removed / ml at \( t = 60 \) min | \( \% \) liquid products treatment | end- | gaseous products concentration / ppm at \( t = 60 \) min |
|---------|--------|---------------------------------|-----|--------------------------------------------------|
| Batch   | 140    | 0.10                           | > 0.64 | 712.4 ± 28.5 |
| Recycling | 220    | 0.63                           | < 0.20 | 1546.9 ± 61.9 |
| Batch   | 140    | 9.96                           | < 1.10 | 960.3 ± 38.4 |
| Recycling | 220    | 28.2                           | < 0.50 | 5287.05 ± 206.2 |

Figs. 2 and 3 show the time evolution of end-products in the gas-phase in both the batch and recycling treatments for treatment in humid argon and nitrogen, respectively. For treatment in both humid nitrogen and argon, there is increased yield of gaseous products in the recycled mode with a 450% increase in the case of humid nitrogen. For argon, the gaseous products are dominated by evaporated dodecane in the batch mode and also include smaller hydrocarbons especially methane. CO is the dominant oxidation product. Processing in humid nitrogen shows additional nitrogen-containing products viz. HCN and NO. \( \text{C}_2\text{H}_4 \) is a dominant end-product in both batch and recycling modes with CO being the major product in the batch mode and HCN being significant in the case of recycling.

During the recycling \( \text{N}_2/\text{H}_2\text{O} \) or \( \text{Ar}/\text{H}_2\text{O} \) plasma-liquid treatment of dodecane, liquid samples were collected at time intervals of 5, 20, 30, 40, 50 and 60 min, in order to characterise the by-product formation in the liquid during treatment time. In both conditions, the colour of the oil was turning gradually to yellow indicating the formation of liquid by-products. In addition, soot was also formed, particularly in case of the \( \text{N}_2/\text{H}_2\text{O} \) treatment.

![Fig. 2. Gaseous products comparison between Ar/H2O GAD batch and recycling, \( P_{in} = 140 \) W.](image)

![Fig. 3. Gaseous products comparison between N2/H2O GAD during 60 min of batch and recycling treatment, \( P_{in} = 200 \) W.](image)

The liquid products identified in the crude samples after the \( \text{N}_2/\text{H}_2\text{O} \) plasma batch treatment of dodecane, are similar to those observed earlier in the case of the batch treatment. These are alkenes such as decene (\( \text{C}_{10}\text{H}_{20} \)), undecene (\( \text{C}_{11}\text{H}_{22} \)), alcohols such as tridecanol (\( \text{C}_{13}\text{H}_{28} \)), tetradecanol (\( \text{C}_{14}\text{H}_{30} \)), pentadecanol (\( \text{C}_{15}\text{H}_{32} \)), hexadecanol (\( \text{C}_{16}\text{H}_{34} \)) and triphenylmethanol (\( \text{C}_{19}\text{H}_{16} \)). The aliphatic ester of bis(3-ethylhexyl) adipate (\( \text{C}_{22}\text{H}_{42} \)) is also identified. These species are also seen in case of the \( \text{Ar}/\text{H}_2\text{O} \) recycling treatment of dodecane, as well as some higher oxidation level products such as undecanols and isomers of \( \text{C}_{12}\text{H}_{24} \).

The crude samples were subjected to liquid column chromatography and polar fractions were collected for IR and GC-MS analysis. Major products formed in all cases are decanol, tetradecanol, pentadecanol, hexadecanol, the aliphatic ester of bis(3-ethylhexyl) adipate and the bis(6-methylheptyl) phthalate ester. In both \( \text{N}_2/\text{H}_2\text{O} \) and \( \text{Ar}/\text{H}_2\text{O} \) plasma treatment at 5 min, alcohol products seems to have overall high abundance, while the production of esters seem to be more important at longer
treatment time up to 60 min. This could indicate that light molecules formed initially in the treated dodecane can subsequently lead to heavier higher oxidation state molecules.

4. Plasma Chemistry

The plasma chemistry involved in the formation of the gaseous and liquid phase chemistry is complex. We have recently studied the chemistry of the gas-phase degradation of dodecane using a packed-bed plasma reactor [2] but the chemistry of plasma-liquid systems is complicated by the existence of three reaction regions viz. gas-phase, liquid-phase and the gas-liquid interface where a range of physical and chemical phenomena played roles of varying importance. Electron impact reactions or hydrogen abstraction reactions from N, OH or O radicals formed in the discharge in different conditions can initiate the dodecane fragmentation leading to fragments varying from methyl radicals to undecyl radicals. Recombination reactions between these radicals can lead to the formation of heavier alkanes as final products. In a dry N₂ or Ar plasma, a reducing environment rich in H atoms is expected and further hydrogen abstraction from alkyl radicals can lead to the formation of alkenes and molecular hydrogen, as shown below. Under humid conditions, the hydroxyl radical formed in the discharge by water dissociation can add to the alkyl radicals to form the respective alcohols.

Atomic oxygen also identified in humid conditions can add to alkyl radicals leading to alkoxy radicals which can then form alcohols if they are hydrogenated, aldehydes or ketones if dehydrogenated and ethers in they react further with another alkyl radical where R₁, R₂ could be alkyl radicals or hydrogen.

5. Conclusions

The plasma degradation of liquid dodecane has been studied using gliding arc discharge, as a batch and recycling treatment. Results show that there are differences between the gas chemistry during the plasma-liquid treatment of dodecane and the treatment of gaseous dodecane. The selectivity of the gaseous products can change, due to the plasma-liquid interactions. The reactive species formed in plasma can diffuse into the liquid interface to initiate reactions which could mainly breakdown dodecane to lighter gaseous products but also form heavier products remaining in the bulk liquid. Liquid-based chemistry presents a scenario largely dominated by diffusion and solvation effects. This differs from the gas-phase chemistry in plasmas where the species behave as isolated entities and the reactions are mainly determined by their reaction activation energies.

A wide range of liquid products have been identified such as heavier saturated or unsaturated hydrocarbons both aliphatic and aromatic, and oxidation products mainly alcohols, but also aldehydes, ketones and esters. In the case of Ar plasma, the abundance of aldehydes and ketones is higher than alcohols, in contrast to the N₂ plasma liquid products, where alcohols abundance is higher. In the latter case, it is possible that the oxidation reaction rates are decreased, due to slower diffusion rate of the reactive species caused by dynamic vaporisation.

The recycling treatment of dodecane creates a direct plasma-liquid treatment, which increases the reactivity and changes the selectivities of the gaseous products. Compared to the batch treatment results, the degradation efficiency for both Ar/H₂O and N₂/H₂O plasma is increased by a factor of 4.2 and 4.9, respectively. Liquid analysis of samples from different treatment times shows that similar products are formed, with no significant change during the treatment time.

Overall, the study of gliding arc plasma-liquid treatment of dodecane shows promising results for the organic liquid waste treatment. We find that humid N₂ plasma appears more favourable than Ar giving a higher degradation rate, destroying a larger volume of oil and leaving lower concentration of residual end-products in the liquid. On the other hand, humid Ar plasma creates lower gasification and promotes the liquid chemistry. This research field should be further explored for selective liquid treatment applications. Our results show that a potential recycling treatment would increase significantly the rate of the process.

6. Acknowledgement

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7. References
