

## Kinetics of gasoline vapor removal in a Poraver filled biofilter

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**ABSTRACT.** The objective of this study was to evaluate the kinetic constants of gasoline degradation in waste gases using a bench-scale biofilter with ID 100 mm and a bed height of 750 mm. The overall, aliphatic and aromatic fractions were analyzed separately. The concentrations of pollutants were measured at various points down the bio-reactor to give a concentration profile. The packing material was Poraver (Dennert Poraver GmbH, Germany) with a grain size of 8 – 16 mm. The inlet concentration was kept constant at 250 mg m<sup>-3</sup> and the biofilter was loaded by air flow rate.

The results showed, as expected, that increasing the residence times improved the removal rates. The aromatic components were removed more rapidly and more completely than the aliphatic compounds. To determine the most appropriate form of the Ottengraf model, following criterion was used: minimized the coefficient of determination of the fitted values of the reaction constants. The zero order kinetic model was superior. (For aliphatic compounds, use the reaction limited equation and for the aromatic components, diffusion limited was marginally better.)

### 1 INTRODUCTION

Atmospheric contamination with gasoline vapor is a general phenomenon around the world.

The vapors are adsorbed on granular activated carbon during car tank filling at some gas stations in a few states in the USA. To reduce these vapor losses, biofiltration procedure can also be effectively applied.

Biofiltration is a useful and economic way to purify air streams contaminated with volatile organic compounds (Devinny *et al.*, 1999). It is relatively cheap in comparison to conventional techniques such as incineration, condensation, absorption or adsorption (Chang and Lu 2003; van den Ban *et al.*, 2003). Generally, biological gas treatment is environmentally friendly, performed at ambient temperatures, and it does not generate nitrogen oxides or secondary waste streams. It is particularly applicable when high volumetric rates and low inlet concentrations are involved (Choi *et al.*, 2004).

Ottengraf's (Ottengraf 1986; Ottengraf 1987) equations were used to describe the pollutants' degradation along the bed height. These are relatively simple, steady-state models with an analytical solution.

Zero order kinetics with reaction limitation gives:

$$\frac{C_g}{C_{gi}} = 1 - \left[ \frac{hK_0}{C_{gi}u_g} \right] \quad (1)$$

Zero order kinetics with diffusion limitation:

$$\sqrt{\frac{C_g}{C_{gi}}} = 1 - \frac{h}{u_g} \sqrt{\frac{K_0 D \alpha}{2mC_{gi}\delta}} \quad (2)$$

First order kinetics:

$$\ln \left[ \frac{C_g}{C_{gi}} \right] = \frac{-hK_1}{mu_g} \quad (3)$$

All these equations were used to linearize the degradation concentration profiles. This makes it easy to determine the (grouped) kinetic constants ( $k$  or  $K$ ) from the gradients of the straight-line graphs.

Zero order kinetics with reaction limitation:

$$K_0 \quad (4)$$

Zero order kinetics with diffusion limitation:

$$k_0 = \sqrt{\frac{K_0 D \alpha}{2m\delta}} \quad (5)$$

First order kinetics:

$$k_1 = \frac{K_1}{m} \quad (6)$$

## 2 MATERIALS AND METHODS

The biofilter was made of glass with an internal diameter of 100 mm a bed height of 750 mm. The concentration of pollutants was measured at bed heights of 0 ( $C_{in}$ ), 10, 27, 44, 61 and 75 cm ( $C_{out}$ ). The packing material was Poraver (Dennert Poraver GmbH, Schlusselfeld, Germany) with a grain size of 8 – 16 mm.

The biofilter was equipped with six sampling ports along the bed height. This configuration permits measurement of concentration profile through the reactors. Biofilter operating conditions were: up flow mode (ID 100), temperature 21 – 23 °C. Experimental biofilter is shown in figure 1.

The mixed microbial culture used in biofilter was obtained from a biofilter that was used for more than two years of operation (for styrene removal from waste air in our laboratory).

The GC-MS (Agilent 6890 with MSD 5973) analysis of gasoline 95 showed the following average composition: 46.7 % of aliphatic components and 52.3 % of aromatic components. The gasoline in the gas phase was determined using an Agilent 6890 N gas chromatograph equipped with a flame ionization detector (FID). Operating conditions were: initial temperature, 90 °C; initial hold time, 2 min; ramp, 45 °C.min<sup>-1</sup>; final temperature, 150 °C; final hold time, 3.2 min; FID temperature, 250 °C.

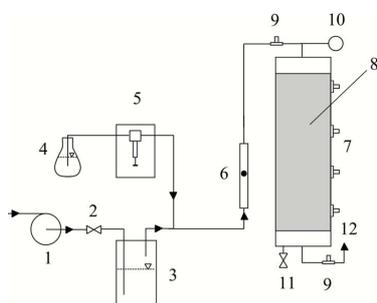


Figure 1. Schematic of the experimental apparatus: 1 - blower, 2 - needle valve for flow rate control, 3 - humidification vessel, 4 - vessel with gasoline, 5 - syringe pump, 6 - rotameter, 7 - biofilter with four sampling ports, 8 - packing, 9 - inlet/outlet sampling ports, 10 - manometer, 11 - valve for leachate, 12 - outlet.

### 3 RESULTS AND DISCUSSION

The results showed, as expected, that increasing the residence times improved the removal rates (Figures 2 - 4). Significant influence of residence time on removal efficiency hydrocarbons was reported by several authors (Morales *et al.*, 1998; Dapasquier *et al.*, 2002). It is evident especially in case of degradation of aliphatic hydrocarbons.

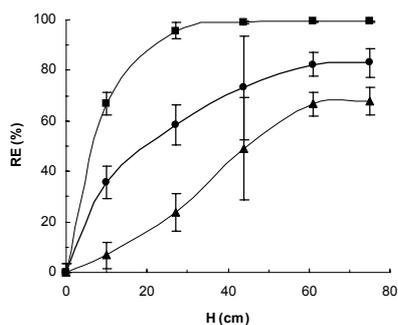


Figure 2. Removal efficiency along the bed height at EBRT of 26,7 min.

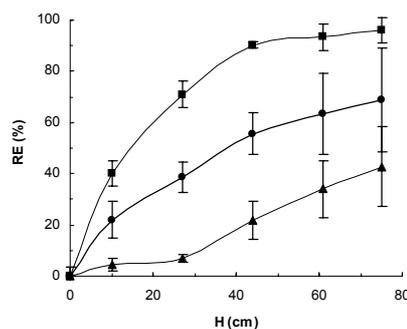


Figure 3. Removal efficiency along the bed height at EBRT of 13,4 min.

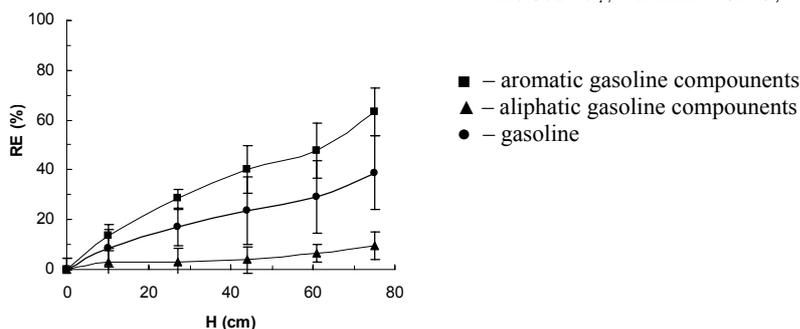


Figure 4. Removal efficiency along the bed height at EBRT of 6,7 min.

The aromatic components were removed more rapidly and more completely than the aliphatic compounds. It can be seen effective degradation of aliphatic compounds starts when removal efficiency of aromatic compounds exceeds approximately 75 %

(comparison of Figures 2-4). Results of Leson and Smith found the same tendency in degradation individual hydrocarbons or their mixtures (aromatic vs. aliphatic hydrocarbons).

We used the coefficient of variation, (defined as the ratio of standard deviation to mean,  $S_K/K$ ) as the criterion for choosing the best equation – the smaller this is, the smaller is the variation of kinetic constant. Applying the criterion, it can be seen that first order kinetics gave a reasonable fit to total gasoline degradation (Table 1). Instead of this, zero order kinetics gave more suitable fit to aliphatic (slightly better equation 1) and aromatic (slightly better equation 2) gasoline components degradation (Tables 2 and 3).

Table 1. Calculate model constants and their statistic evaluation for total gasoline degradation.

EBRT	$K_0$	$k_0$	$k_1$
26.7 min	4,8759	0,2307	0,0463
13.4 min	8,3759	0,3502	0,0602
6.7 min	9,0706	0,3238	0,0465
average (K)	7,4408	0,3016	0,0510
standard deviation ( $S_K$ )	2,2483	0,0628	0,0080
$S_K/K$	0,3022	0,2082	0,1562

Table 2. Calculate model constants and their statistic evaluation for aromatic gasoline components degradation.

EBRT	$K_0$	$k_0$	$k_1$
26.7 min	7,6781	0,6056	0,2378
13.4 min	5,5405	0,4597	0,2006
6.7 min	8,1374	0,4361	0,0955
average (K)	7,1187	0,5005	0,1780
standard deviation ( $S_K$ )	1,3859	0,0918	0,0738
$S_K/K$	0,1947	0,1834	0,4147

Table 3. Calculate model constants and their statistic evaluation for aliphatic gasoline components degradation.

EBRT	$K_0$	$k_0$	$k_1$
26.7 min	2,4714	0,1403	0,0327
13.4 min	2,8353	0,1445	0,0297
6.7 min	0,9331	0,045	0,0087
average (K)	2,0799	0,1099	0,0237
standard deviation ( $S_K$ )	1,0097	0,0563	0,0131
$S_K/K$	0,4855	0,5119	0,5518

#### 4 CONCLUSIONS

- Higher value of residence time improved the removal rate.
- The aromatic components were removed more rapidly and more completely than the aliphatic compounds.
- First order kinetics gave a reasonable fit to total gasoline degradation.
- Zero order kinetics gave a reasonable fit to aliphatic and aromatic compound degradation.

## NOMENCLATURE

$S_K$	standard deviation
RE	removal efficiency, %
EBRT	empty bed residence time, min
$C_g$	gas concentration, $\text{mg}\cdot\text{m}^{-3}$
$C_{gi}$	inlet gas concentration, $\text{g}\cdot\text{m}^{-3}$
$D$	liquid phase diffusion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
$h$	filter bed height, m
$K_0$	zero order reaction constant
$K_1$	first order reaction constant
$m$	gas liquid partition coefficient
$Q$	air flow rate, $\text{m}^3\cdot\text{s}$
$u_g$	superficial velocity, m/s
$\alpha$	ratio of surface area to volume, $\text{m}^{-1}$
$\delta$	biolayer thickness, m

## 5 ACKNOWLEDGEMENT

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