# THERMODYNAMIC ANALYSIS OF DETONATION-ASSISTED GASIFICATION OF ORGANOCHLORINE WASTES

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**Abstract:** The optimal thermodynamic conditions have been determined for the allothermal noncatalytic steam — carbon dioxide (hereinafter referred to as detonation-assisted) gasification of various organochlorine compounds (OCC) in an environment of high-temperature gaseous detonation products expanded to atmospheric pressure, yielding nontoxic valuable syngas and commercial hydrochloric acid. Thermodynamic modeling indicates that this thermal utilization process for OCC ensures complete carbon conversion without the formation of soot or hydrocarbons, achieving a dry syngas yield of up to 5.7 $Nm^3/kg$ and a cold gas efficiency of up to 138%. For the utilization of highly chlorinated feedstocks (exceeding 70 %(wt.) chlorine) or feedstocks with an unsaturated molecular structure, a co-feeding method of OCC and external hydrocarbons (using $C_4H_8O_2$ as an example) is justified to suppress the formation of major ecotoxicants such as $Cl_2$, $COCl_2$, and $C_2Cl_2$. To achieve complete suppression of these toxic compounds, it is sufficient for the mass fraction of $C_4H_8O_2$ in the mixture not to exceed 0.33. Regarding other chlorine-containing ecotoxicants, including dioxins, their concentrations in the equilibrium gasification products remain negligible even without dilution. It is demonstrated that for all considered OCCs (both in pure form and diluted with ethyl acetate $C_4H_8O_2$), chlorine binds exclusively into hydrogen chloride (HCl), with all hazardous emissions remaining below the conventional limit of 0.1 ppm. A chlorine capture algorithm has been substantiated, based on dissolving the generated HCl in the condensate of residual or externally supplied water vapor as the gasification products cool down to 293 K. The proposed technology represents an efficient and environmentally safe alternative to expensive plasma-based methods for the disposal of toxic OCCs.

**Keywords:** organochlorine wastes; steam–carbon dioxide gasification; detonation products; thermodynamic modeling; syngas; environmental safety; hydrochloric acid

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## Figure Captions

**Figure 1** Process flow diagrams of gasification processes implemented in the Aspen Plus software package: (*a*) steam gasification of feedstock (used for model validation); and (*b*) steam–carbon dioxide gasification in a stream of detonation products of a triple methane – oxygen – water vapor mixture expanded to atmospheric pressure

**Figure 2** Calculated dependences of temperature and composition of $n$-hexadecane gasification products by detonation products of a stoichiometric methane–oxygen mixture without water vapor addition on the specific consumption of feedstock $m$; equivalence ratio $\Phi = 1$; water vapor dilution $\alpha = 0$

**Figure 3** Calculated dependences $m(\Phi)$ at $\alpha = 0$ (*a*) and $m(\alpha)$ at $\Phi = 1$ (*b*) at the lower (LL), upper (UL), and extended upper (EUL) limits of the operating window during detonation gasification of $n$-hexadecane

**Figure 4** Calculated dependences of process temperature and equilibrium composition of chlorohexadecane gasification products on the specific consumption of feedstock $m$; $\Phi = 1$; $\alpha = 0$

**Figure 5** Calculated dependences of the specific consumption of feedstock $m$ at the LL (*1*), UL (*2*), and EUL (*3*) of the operating windows for detonation-assisted gasification of moderately chlorinated hydrocarbons from Table 1

**Figure 6** Calculated equilibrium compositions (including radicals in the gasifying agent) of uncooled gasification products of moderately chlorinated hydrocarbons at the UL of the operating windows

**Figure 7** Calculated lower heating values of dry syngas (including radicals in the gasifying agent) obtained during detonation-assisted gasification of moderately chlorinated hydrocarbons at the LL (*1*), UL (*2*), and EUL (*3*) of the operating windows

**Figure 8** Calculated dry gas yields (*a*), cold gas efficiencies (*b*), and net energy efficiencies (*c*) (including radicals in the gasifying agent) during detonation-assisted gasification of moderately chlorinated hydrocarbons at the LL (*1*), UL (*2*), and EUL (*3*) of the operating windows

**Figure 9** Calculated equilibrium compositions (including radicals in the gasifying agent) of uncooled gasification products of moderately chlorinated hydrocarbons at $m = m_{\text{sat}}$, i. e., under conditions where, upon cooling the gasification products to $T = 293$ K, all formed hydrogen chloride dissolves in the residual water vapor condensate, forming a saturated aqueous solution of hydrochloric acid

**Figure 10** Calculated dependences of the $C_2Cl_2$ mass yield $M_{C_2Cl_2}/M_{OCC}$ (*a*) and volume fraction (*b*) with cooled (dry) syngas on the mass fraction of the diluent ($C_4H_8O_2$) in the $OCC + C_4H_8O_2$ mixture for all chlorinated hydrocarbons from Table 1, including highly chlorinated hydrocarbons

# Table Captions

**Table 1** Chemical compounds examined in the study

**Table 2** Comparison of calculated and experimental equilibrium compositions of syngas obtained during catalytic steam reforming of $n$-hexadecane at atmospheric pressure

**Table 3** Comparison of calculated and experimental equilibrium compositions of syngas obtained during catalytic steam reforming of chlorinated hydrocarbons at atmospheric pressure

**Table 4** Equilibrium temperatures and compositions of detonation products at the inlet of the gasifier reactor

**Table 5** Characteristics of gasification products of moderately chlorinated hydrocarbons at a specific feed rate $m_{\text{sat}}$ corresponding to the complete dissolution of HCl in water vapor condensate at $T = 293$ K and $p = 0.1$ MPa

**Table 6** Mass yields and volume fractions of $Cl_2$, $COCl_2$, and $C_2Cl_2$ in gasification products, calculated at the UL of the corresponding operating windows for pure chlorinated hydrocarbons and those diluted with $C_4H_8O_2$

**Table 7** Comparison of plasma and detonation-assisted gasification

**Table 8** Thermodynamic and integral performance parameters of the $n$-hexadecane gasification process at the operating window boundaries

**Table 9** Thermodynamic and integral performance parameters of the gasification process of moderately chlorinated hydrocarbons at the operating window boundaries

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