

Stability of Olefin-Containing Process Gases as an Alternative Fuel for Gas Turbines

P. A. Glaude,* R. Fournet, and V. Warth

Département de Chimie-Physique des Réactions, UMR 7630 CNRS, INPL 1, rue Grandville, 54000 Nancy, France

M. Molière

General Electric Energy Product France, 20 rue du Maréchal Juin, 90007 Belfort, France

The undesirable polymerization of unsaturated species yielding gums and deposits is likely to disturb many processes or systems using hydrocarbons, in particular motor engines, industrial production of olefins, or gas turbines units. To allow the determination of a safe margin of operation, a detailed chemical kinetic approach is proposed to develop a model of reaction applicable in the low-temperature/high-pressure range with very low conversion rate. A model for a mixture of alkanes, olefins, conjugated diolefins, and alkynes is described and used to simulate the practical case of a gas turbine fed with a petrochemical gas. The factors influencing the polymerization rate are analyzed. The presence of diolefin, especially propadiene-like ones, is a critical parameter. Alkynes also increase dramatically the formation of gums. A coupling effect between diolefins and monoolefins or alkynes is established. Temperature is the most sensitive reactor parameter. Correlations are proposed between the rate of the polymer formation and the composition of the mixture.

1. Introduction

In a number of industrial processes, uncontrolled polymerization of olefins is known to be a potential source of operation problems, including equipment fouling and, in most severe cases, unit shutdown. For example, parasite polymerization occurs in fuel tanks at room temperature because of a slow oxidation mechanism^{1,2} that yields soluble gums and heavier oxygenated polymers that can deposit on the walls.³ In spark-ignited gas engines, olefin-containing fuels lead to the formation of polymer by gum deposition inside fuel nozzles under the high pressure and temperature conditions of injection.⁴ The effect is enhanced in the presence of fuel impurities, such as compounds containing nitrogen or sulfur heteroatoms.^{5,6} In petrochemistry, olefin production equipment (including compressors, separators, condensers, or distillation columns) may face similar issues and experience serious production losses.⁷ Tubular reactors in polymerization facilities are designed to be ideal polymerization reactors. However, in practice they are of little use due to disturbing polymer layers that preferentially form and stick on tube walls, which are the hottest reactor zones.⁸

Among the industrial processes, gas turbines may be concerned with the gum when using olefin-containing fuels. Throughout the history of combustion engines, the gas turbine stands out as the most fuel-flexible prime mover in the field. The gas turbine is suited for a rich portfolio of gaseous fuels that includes natural gas, liquefied petroleum gas, coal- and biomass-derived syngases, and a great variety of process gases with diverse compositions (hydrogen, carbon monoxide, olefins, etc.) that could be valorized for energy production.

Process gas fuels provide a promising array of alternative fuel opportunities in the major sectors of industry, such as the coal, oil, and gas; steel; and chemical and petrochemical branches. In an increasingly uncertain fuel environment, this significant match between gas turbine capabilities and the energy schemes of industrial plants can lead to further uses.

An emerging family of process gases for gas turbine applications can be found in the olefin-rich off-gases of petrochemical units. In general, such gas streams are complex mixtures of C₁–C₄ hydrocarbons, including paraffins, olefins, diolefins, and sometimes alkynes. During the first attempts to use such olefin-rich fuels for combustion, the delicate problem of reputedly “unpredictable” polymerization of olefins in fuel gas circuits has been encountered, which caused flow restriction or even unit shutdown. With the increasing potential of such fuels in the power-generation field, it looked desirable to have a better fundamental knowledge of the polymerization risk and to define some safe criteria for gas turbine applications.

Until now very few studies have been devoted to this problem, and they have been focused mainly on automotive fuels. Moreover, they have been limited to qualitative considerations without any attempt to predict or model the appearance of polymerization. However, a number of key factors have been identified: pressure and temperature are the most sensitive parameters, and some relationships have been demonstrated between the chemical composition of the fuel and the amount of gum formation.^{5,9} The different hydrocarbons contained in a fuel can be ranked according to their decreasing reactivity in gum formation: diolefins, aromatic compounds with an unsaturated chain linked to the ring, monoolefins, other aromatic compounds, isoparaffins (branched alkanes), cyclic alkanes, and paraffins.

* To whom correspondence should be addressed. Tel.: 33 383 17 51 01. Fax: 33 383 37 81 20. E-mail: glaude@ensic.inpl-nancy.fr.

The most favorable species for the gum formation are diolefins. Experiments also showed a synergetic effect between both mono- and diolefins when present together.⁵ In such a case, a larger amount of gums have been obtained than that yielded with one only component. The chemical structure of the olefin is also of importance.⁹ Olefins can be ranked according to their decreasing reactivity in gum formation: dicyclic olefins, cyclic olefins, olefin with a ramification on the double bond, branched olefins, heavy linear olefins, light linear olefins.

The present work focuses on the prediction of the risk of polymerization of unsaturated hydrocarbons in process gases that are used as fuels for industrial gas turbines. A kinetic modeling approach has been developed in order to represent the reactions of the different chemical components in the mixtures.

2. Methodology

The process gases used as fuels in gas turbines are generally mixtures of paraffins (propane, butanes) and olefins (propene, butenes) with traces of diolefins and alkynes. As discussed below, the typical temperature and pressure ranges of gas turbine applications (10–30 bar and 100–400 °C, respectively) represent much milder conditions than those set in industrial polymerization processes. Therefore, they lead to reaction rates that are smaller by several orders of magnitude. This circumstance, along with the multitude of reaction products and intermediates, discouraged the use of an experimental approach that would have resulted in intricate analytical issues and required delicate and tedious experiments with long accumulation times. Therefore, a modeling approach has been first selected. The slow reaction rates also required a detailed kinetic rather than a global polymerization model, extrapolation of which to such a slow reactivity would be hazardous. A gas phase detail kinetic mechanism involves elementary reactions, the rates of which are only dependent on the pressure, temperature, and concentrations of the reactants. Such detailed kinetics provide moreover a complete distribution of the individual polymerization products according to temperature and reactant concentrations, while the overall polymerization rate can be calculated by summing the masses of all depositable polymers formed by unit of time. The surface chemistry and the possible catalytic effect of some atoms at the walls have not been considered here.

3. Kinetic Modeling

The chemical mechanisms describing the thermal evolution of process gas were developed by a dedicated computer-aided automatic generation program. This approach was required because of the large number of intermediate species and multiple reactions that were possible due to the coupling between all the species present at a given time (reactants plus intermediate products). The model is generated with the help of EXGAS, a dedicated software developed in the DCPR in Nancy, France,¹⁰ to model hydrocarbon oxidation and pyrolysis. EXGAS automatically generates all the reactions involved by the hydrocarbons that are present as initial reactants or as intermediate products in the evolving system. The mechanism includes all the elementary steps corresponding to the reaction types

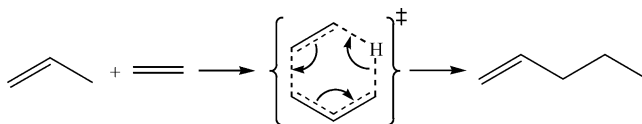
specified by the user. Their kinetic data are evaluated using structure–reactivity relationships deduced from the literature^{11,12} or thermochemical methods.¹³ The thermochemical properties of the species (i.e. enthalpy of formation, entropy, and heat capacity) are calculated using THERGAS software, which relies on group additivity methods.^{13,14} The mechanism follows the same standards as the CHEMKIN II software package¹⁵ used to model ideal laboratory reactors.

The system EXGAS has been first developed for modeling the oxidation and the high temperature thermal decomposition of hydrocarbons. Therefore, many reaction pathways have not been included in its initial form, which can play an important role in the low-temperature and high-pressure conditions of the polymerization, such as molecular reactions or numerous additions of free radicals on the double bond of the olefins. The software was modified to take into account these particular polymerization reactions occurring in the low-temperature range as required by the case under study. To that end, two reaction channels have been considered: the molecular reaction route and the chain radical mechanism.

In this paper, rate constants will be written in the Arrhenius form. R^\bullet will represent an alkyl free radical, Y^\bullet an allylic (resonance stabilized) radical, and V^\bullet a vinylic radical (active center on an unsaturated C-atom). We also distinguish the reactivity of a primary, secondary, tertiary, or quaternary C-atom, which is bonded to one, two, three, and four C-atoms, respectively. H-atoms are named also primary, secondary, or tertiary when they are bonded to a primary, secondary, or tertiary C-atom, respectively.

Molecular Reaction Routes. Olefins can react within two reaction schemes, as outlined below.

Ene Reaction. Two unsaturated molecules condense into a new olefin. For instance, propene and ethylene can react together by an ene reaction as follows:



The rate constant of the reaction between two molecules of propene has been measured by Richard and Back:¹⁶

$$k = 7 \times 10^9 \exp\left(-\frac{37\,000 \text{ cal mol}^{-1}}{RT}\right) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

When propene reacts with larger molecules, the preexponential A factor decreases because of the steric hindrance. Thus, the addition of propene or another monoolefin to a larger olefin is supposed to be 2 times slower. If the olefin involves two double bonds, the A-factor is multiplied by a factor of 2 (reaction of an olefin with a polyolefin).

Moreover, the gas-phase ene reactions involving a conjugated diolefins must be distinguished. The addition of 1,3-butadiene to propene is easier¹⁷ than that of a regular olefin:

$$k = 5 \times 10^9 \exp\left(-\frac{31\,000 \text{ cal mol}^{-1}}{RT}\right) \quad (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

Table 1. Rate Constants of the Ene Reaction of Monoolefins and Conjugated Diolefins

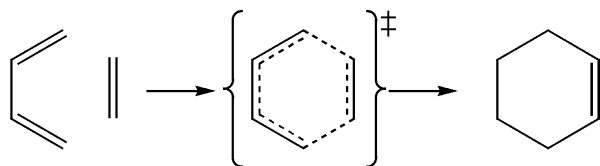
	A ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	E_a (cal mol^{-1})
$\text{C}_3\text{H}_6 + \text{C}_3\text{H}_6$	7×10^9	37 000
monoolefin + monoolefin	3.5×10^9	37 000
monoolefin + polyolefin	7×10^9	37 000
$\text{C}_4\text{H}_6 + \text{C}_3\text{H}_6$	5×10^9	31 000
conjugated diolefin + monoolefin	2.5×10^9	31 000
conjugated diolefin + polyolefin	5×10^9	31 000

Table 2. Rate Constants of the Diels–Alder Reaction between 1,3-Butadiene and Olefins

	A ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	E_a (cal mol^{-1})
$\text{C}_4\text{H}_6 + \text{C}_4\text{H}_6$ or C_3H_6	9.7×10^9	24 500
$\text{C}_4\text{H}_6 + \text{monoolefin}$	2.3×10^9	24 500
$\text{C}_4\text{H}_6 + \text{polyolefin}$	4.6×10^9	24 500

Some correlations have also been deduced by correcting the preexponential factor for the addition of conjugated diolefins to larger olefins. Rate constants are summarized in Table 1.

Diels–Alder Reaction. This reaction consists of the condensation of a conjugated diolefin and a monoolefin and yields a cyclic monoolefin through a six-member concerted transfer. In the following example, ethylene and 1,3-butadiene produce cyclohexene:

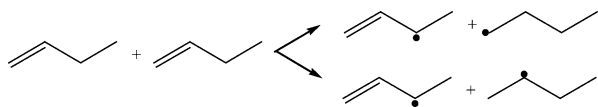


These molecular reactions are essential under the conditions being considered due to their relatively low activation energies.

The rates of the reactions between two molecules of 1,3-butadiene and between 1,3-butadiene and cyclohexene have been measured by Huybrechts et al.¹⁸ We have used the same rate for the reaction with propene as that with butadiene; we corrected the preexponential factor of the Diels–Alder condensation of a diolefin with a larger olefin to fit the experimental value of the reaction between 1,3-butadiene and cyclohexene. Table 2 lists the different rate constants.

Chain Radical Mechanism. The following reaction types are considered in the model.

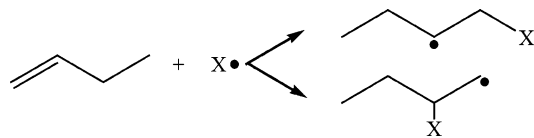
Bimolecular Initiation. An H-atom is transferred to an unsaturated molecule yielding two free radicals. Only reactions leading to a resonance stabilized free radical are considered in the mechanism, because of their low activation energy. In the following example, 1-butene can react by bimolecular initiation to give the resonance-stabilized 3-butenyl and an alkyl free radical:



Kinetic parameters are self-generated by the KINGAS software¹⁹ based on thermochemical methods proposed by Benson.¹³

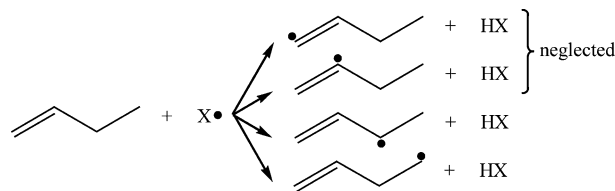
Addition of a Free Radical on an Unsaturated Bond. The addition of free radicals on double or triple bonds is a specific reaction of unsaturated hydrocarbons. This reaction yields a new radical. It is worth noting

that all the free radicals created in the mechanism can react by addition. This is a consequence of the low temperature of the process. A radical X^\bullet can add on both sides of the unsaturated bond and produces two isomers.



The reaction rate depends of the reactivity of the free radical and that of the multiple bond. Rate constants depend thus on the type of adding radical and the type of new radical that is yielded. Values are partly taken from Heyberger et al.¹² or have been estimated in this work for the missing ones (addition of allylic and vinylic free radicals, noted Y^\bullet and V^\bullet , respectively; addition on the conjugated dienes yielding a resonance stabilized radical Y^\bullet ; addition of free radicals on a triple bond yielding a vinylic radical V^\bullet). The new estimations are based on a literature review and on correlations between structure and reactivity. Table 3 presents the rate parameters.

H-Abstraction. An H-atom is abstracted from a molecule by a X^\bullet free radical. Three different kinds of H-atom can be abstracted and yield alkyl, vinyl, or resonance-stabilized free radical, respectively. The abstractions of H-atoms bonded to an unsaturated carbon atom are neglected because of their high activation energy and the low temperature except in the case of a conjugated diene yielding a resonance stabilized Y^\bullet radical.



The rate parameters come partly from Heyberger et al.¹² and from estimations made in this work; the new values are mainly based on the correlations proposed by Ranzi et al.²⁰ Table 4 displays all the structure–reactivity relationships used for the abstraction of the different types of H-atom by the different types of free radical.

Termination. The combination of two radicals produces a molecule. Only resonance-stabilized radicals are involved in this step. The others can react faster by addition or H-abstraction. The rate constant is calculated by KINGAS,¹⁹ on the basis of the modified collision theory.¹³

Other radical reactions, such as radical decomposition, are not taken into account because of their very slow rates under the low-temperature conditions.

A detailed description of all reactions and species leads to a mechanism size that is incompatible with simulation. Indeed, each unsaturated radical can appear in the form of as many isomers as its number of carbon atoms allows. The mechanism must thus be reduced, which is accomplished by lumping the chemical species. All the compounds having the same formula and the same chemical functions are grouped in a single lumped species. For each globalized species, the number of double and triple bonds and rings is specified. In the case of the free radicals, one distinguishes alkyl, vinyl,

Table 3. Rate Constants of the Addition of Free Radicals on Multiple Bonds, in the Modified Arrhenius Form $AT^b \exp(-E/RT)^a$

radical type	CH ₂ =C		RCH=C		R ₁ C(R ₂)=C		C=CC=C (yielding Y)			triple bond	
	A	E _a	A	E _a	A	E _a	A	b	E _a	A	E _a
R [•] _{primary}	1 × 10 ¹¹	7250	9.6 × 10 ¹⁰	8000	2 × 10 ¹⁰	9000	1.6 × 10 ¹¹	0	4970	1 × 10 ¹¹	6990
R [•] _{secondary}	1.3 × 10 ¹⁰	6200	7 × 10 ⁹	7200	3.5 × 10 ⁹	8200	2 × 10 ¹⁰	0	4500	1 × 10 ¹¹	6990
R [•] _{tertiary}	3.1 × 10 ⁹	5890	1.6 × 10 ⁹	6900	8 × 10 ⁸	7900	5 × 10 ⁹	0	4000	1 × 10 ¹¹	6990
Y [•] _{primary}	4 × 10 ¹⁰	17000	2 × 10 ¹⁰	18000	1 × 10 ¹⁰	19000	4 × 10 ¹⁰	0	14500	3.2 × 10 ¹¹	6960
Y [•] _{secondary}	2 × 10 ¹⁰	17000	1 × 10 ¹⁰	18000	5 × 10 ⁹	19000	2 × 10 ¹⁰	0	14500	3.2 × 10 ¹¹	6960
Y [•] _{tertiary}	2 × 10 ¹⁰	17000	1 × 10 ¹⁰	18000	5 × 10 ⁹	19000	2 × 10 ¹⁰	0	14500	3.2 × 10 ¹¹	6960
V [•]	2 × 10 ¹¹	3000	1 × 10 ¹¹	3500	5 × 10 ¹⁰	4000	1.5 × 10 ¹²	-0.17	3240	3.2 × 10 ¹¹	6000

^a $b = 0$ in all cases, except in the case of conjugated diolefins. A is in cm³ mol⁻¹ s⁻¹; E_a is in cal. Primary, secondary, and tertiary radicals are active centers on a C-atom linked to one, two, or three other C-atoms, respectively. Y[•] radicals are resonance stabilized. V[•] radicals are vinylic; i.e., the active center is involved in a double bond.

Table 4. Rate Constants of the H-Abstraction by the Free Radicals^a

free radical type	primary H			secondary H			tertiary H		
	A	b	E _a	A	b	E _a	A	b	E _a
Alkyl H-Atom									
R [•] _{primary}	1.0 × 10 ¹¹	0	13 700	1.0 × 10 ¹¹	0	11 400	1.0 × 10 ¹¹	0	9 800
R [•] _{secondary}	1.0 × 10 ¹¹	0	14 700	1.0 × 10 ¹¹	0	12 400	1.0 × 10 ¹¹	0	10 800
R [•] _{tertiary}	5.0 × 10 ¹⁰	0	15 000	5.0 × 10 ¹⁰	0	12 700	5.0 × 10 ¹⁰	0	11 100
Y [•]	1.4 × 10 ¹¹	0	22 500	1.4 × 10 ¹¹	0	20 200	1.4 × 10 ¹¹	0	18 600
V [•]	5.0 × 10 ¹¹	0	11 500	5.0 × 10 ¹¹	0	9 200	5.0 × 10 ¹¹	0	7 600
Allylic H-Atom (Yielding a Resonance-Stabilized Radical Y [•])									
R [•] _{primary}	1.0 × 10 ¹¹	0	11 400	1.0 × 10 ¹¹	0	9 100	1.0 × 10 ¹¹	0	7 500
R [•] _{secondary}	1.0 × 10 ¹¹	0	12 400	1.0 × 10 ¹¹	0	10 100	1.0 × 10 ¹¹	0	8 500
R [•] _{tertiary}	5.0 × 10 ¹⁰	0	12 600	5.0 × 10 ¹⁰	0	10 600	5.0 × 10 ¹⁰	0	8 800
Y [•]	1.4 × 10 ¹¹	0	20 200	1.4 × 10 ¹¹	0	17 900	1.4 × 10 ¹¹	0	16 300
V [•]	5.0 × 10 ¹¹	0	9 200	5.0 × 10 ¹¹	0	6 900	5.0 × 10 ¹¹	0	5 300
Vinylic H-Atom									
R [•] _{primary}				2.5 × 10 ¹¹	0	19 700	2.5 × 10 ¹¹	0	17 400
R [•] _{secondary}				2.5 × 10 ¹¹	0	20 700	2.5 × 10 ¹¹	0	18 400
R [•] _{tertiary}				2.5 × 10 ¹¹	0	21 000	2.5 × 10 ¹¹	0	18 700
Y [•]				3.5 × 10 ¹¹	0	28 500	3.5 × 10 ¹¹	0	26 200
V [•]				1.2 × 10 ¹²	0	17 500	1.2 × 10 ¹²	0	15 200
Vinylic Allylic H-Atom (Diene Yielding a Resonance-Stabilized Radical Y [•])									
R [•] _{primary}							2.5 × 10 ¹¹	0	15 100
R [•] _{secondary}							2.5 × 10 ¹¹	0	16 100
R [•] _{tertiary}							2.5 × 10 ¹¹	0	16 400
Y [•]							3.5 × 10 ¹¹	0	23 900
V [•]							1.2 × 10 ¹²	0	12 900

^a The values are given per H-atom that can be abstracted. A is in cm³ mol⁻¹ s⁻¹, E_a is in cal.

and allyl (stabilized by resonance) free radicals in order to record their difference in reactivity.

4. Notions of Depositable Products, Liquid and Polymer Phases

The aim of the study is to evaluate, among the overall reaction products, those that can be called “depositable products”, which are likely to deposit in solid or liquid form on walls and reduce free passage in fuel system items (pipes, valves, stop valves, etc). An accurate approach to evaluating depositable products should account for the multicomponent vapor/liquid equilibria and the mechanism of deposition on walls. In a primary approach, however, two simplifying and very conservative assumptions are made:

(1) All reaction products of the gas phase containing more than seven carbon atoms precipitate, regardless of the value of their actual partial pressure (which assumes their vapor pressure equals zero).

(2) The whole precipitated fraction actually deposits on walls and is not swept away by the gas stream.

These assumptions are summarized by the concept of “depositable products”, which is simply defined as the sum of the reaction products.

A study of the physical properties of long chain hydrocarbons has shown that, under the operating conditions, the “depositable products” would be only in the liquid state, since the lightest solid hydrocarbon of the polymer series has more than 100 carbon atoms. However, for the practicality of calculations, we have defined two classes of deposits.

Species comprising more than 10 carbon atoms form the polymer phase, the simulation being stopped more-over at C₂₀ for limiting the size of the mechanisms, even though, as mentioned, these compounds form a viscous liquid and not a solid phase. They are the precursors of the polymer molecules as they can further react, as olefins, between each other in the viscous liquid film (addition/reticulation reactions); the sum of their masses is thus representative of the total solid deposition. Later in this paper, this C₁₀₊ fraction will be referred to as the polymer phase or solid phase

Table 5. Characteristics of the Isothermal Plug Flow Reactor

thermal input	120 MW	gas speed	5 m/s
length	50 m	residence time	10 s
diameter	0.15 m	input temp	415 K
flow rate	1 Nm ³ /s	input pressure	20 bar

The C₇–C₉ compounds are the ones that generate the liquid phase and will be referred to as the liquid phase of the deposit. It is noteworthy that these liquids can also further react on the walls and contribute to an increase of the solid polymer phase. The reasons for distinguishing them from the polymer phase are that they are formed in much greater amounts and they have much higher vapor pressures.

5. Gas Turbine Applications

The generic case considered in this paper is a 40 MW class gas turbine with a thermal input of about 120 MW and a fuel injection pressure (P_{inj}) of 20 bar. When pure gaseous butane (lower heating value (LHV) of 124 MJ/Nm³) is burnt, the gas flow rate is about 1 Nm³/s (flow rates are evaluated under normal conditions, i.e., 0 °C and 101 325 Pa).

Reacting Gas. In practical gas turbine applications, the gas phase to be considered consists of mixtures of propane, propene, *n*-butane, 1-butene, 2-butene, and isobutene as main components; while propadiene and 1,3-butadiene are the most common diolefins, alkynes such as propyne can be present in trace amounts. The gas that enters the fuel circuit feeding the gas turbine is superheated by 28 °C (50 °F) above its boiling point (T_b) in order to prevent the formation of a condensed phase. So its injection temperature is $T_{inj} = T_b + 28$ °C.

Definition and Characteristics of the Reactor. In gas turbine applications, polymerization in the gas fuel system must be avoided. The reactor is defined here as the portion of the gas circuit in which the gas is first superheated and transferred to the gas turbine. At the inlet of the reactor, the fuel gas is taken in its saturated state (conditions T_b , P_{inj}) and at the outlet (the gas turbine fuel nozzles) it has the conditions T_{inj} and P_{inj} . The pipe is heated electrically or by steam; a typical length is 50 m.

With a pipe diameter of 0.15 m, the flow rate of 1 Nm³/s gives a gas speed of 5 m/s and a residence time of 10 s. The calculation of flow characteristics shows a strongly turbulent regime with a Reynolds number above 3×10^6 . Consequently, the time required for superheating is low (1.2 s for pure butane), whatever the superheating means selected. The boundary layer thickness has been evaluated as the ratio between the thermal conductivity of the gas and the convective heat coefficient calculated from the Nusselt number. The calculation gives a very low figure, below 40 μm. One can thus consider the pipe as an isothermal plug flow reactor operating at T_{inj} and P_{inj} .

Selection of Reactor Temperature. The values of T_b and T_{inj} for gasified butane are 387 K (114 °C) and 415 K (142 °C). Since butane has the highest value of T_b among the series of process gas considered (C₃-rich gas mixtures are more volatile), the value of 415 K has been taken as a generic value for T_{inj} as it maximizes the deposition risks. Table 5 summarizes the reactor data.

6. Results

General Trends. To evaluate the validity of the methodology and identify the sensitive parameters of

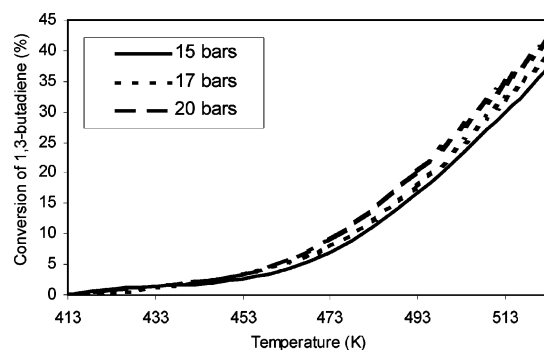


Figure 1. Conversion of pure 1,3-butadiene (in %) vs temperature (T_{inj}) and pressure (P_{inj}) for a residence time of 5000 s.

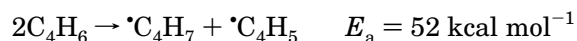
the model, several initial tests were run with some “academic” gas mixtures. The reactor model used here is an isothermal, isobaric, perfectly stirred reactor calculated by the PSR software CHEMKIN II.¹⁵ The use of this simple ideal reactor allowed at this first stage an easy kinetic analysis of the model by exploring the sensitive parameters, even if it was not a realistic representation of the industrial case.

While in gas turbine applications the injection temperature T_{inj} does not exceed 415 K, we have explored, again for conservative reasons, a higher temperature range between 415 K (142 °C) and 520 K (247 °C). The pressure range was 15–20 bar. The time of deposit accumulation has been fixed arbitrarily at 5000 s.

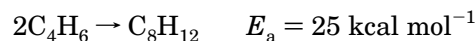
Figure 1 displays the conversion of 1,3-butadiene (defined as the ratio between the converted amount of 1,3-butadiene and the initial amount of 1,3-butadiene) according to temperature and pressure. It shows that the polymerization rate of a pure diolefin can be important as compared to the effect under study and that temperature is a very sensitive parameter, while pressure is not very important in the range studied.

The analysis of the model shows that 1,3-butadiene is mostly consumed by the molecular channel, because molecular cyclizations have a much lower activation energy than radical initiations:

initiation step:



Diels–Alder reaction:



This means that very few radicals are produced. The radical channel, however, is very important for the formation of high molecular weight species, i.e., polymers. Indeed, free radicals are fast polymerization propagators by addition on the double bonds (the activation energy is typically between 6 and 19 kcal/mol), while the molecular product of the Diels–Alder route reacts very slowly in successive molecular steps.

Figure 2 compares the conversion of pure propene and pure 1,3-butadiene. The monoolefin shows no reactivity under these conditions, even at high temperature. Its consumption still occurs by molecular condensation, but the only possible reaction is the ene reaction with a greater activation energy than the Diels–Alder pathway ($E_a = 37$ and 24 kcal mol^{-1} , respectively).

Figure 3 displays a coupling between diolefin and monoolefin in a ternary mixture containing propane or inert gas (helium) added with 0.1% 1,3-butadiene and

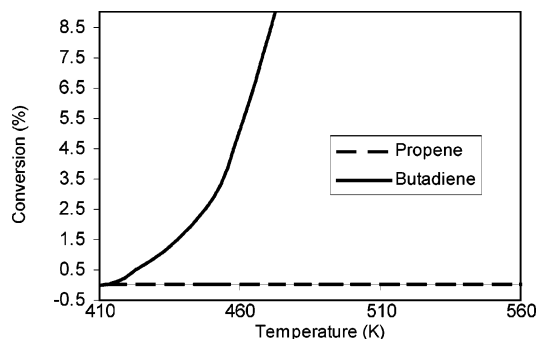


Figure 2. Conversion of propene and 1,3-butadiene vs temperature (T_{inj}) for a residence time of 5000 s and a pressure (P_{inj}) of 20 bar.

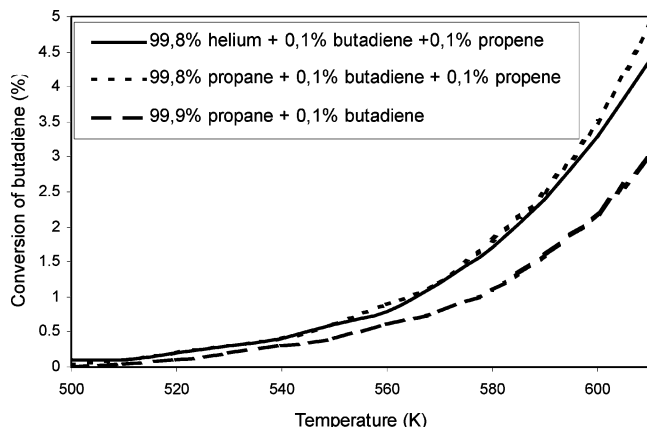
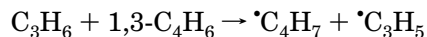


Figure 3. Conversion of mixtures of 1,3-butadiene, propene, propane, or helium vs temperature (T_{inj}) for a residence time of 5000 s and a pressure (P_{inj}) of 20 bar.

possibly 0.1% propene. The reactivity of 1,3-butadiene increases noticeably in the presence of the monoolefin. In contrast, the chemical effect of the alkane is very weak and the corresponding plot virtually overlaps the one involving helium.

Further kinetic considerations show that the enhancement of the reactivity is due to the low activation energy of the particular initiation step for the couple (C_3H_6 , 1,3- C_4H_6) because of the existence of two resonance-stabilized free radicals:



It should be noted that resonance-stabilized radicals react slowly by addition or H-abstraction under these conditions because of their low reactivity (high activation energies involved). They react mainly in combination with each other to yield molecules with 14 or 16 carbon atoms. As previously noted, the molecular route is the major way of consumption of 1,3-butadiene, but the radical way is significant with regard to the formation of polymer (molecules with more than 10 carbon atoms).

Gas Turbine Applications. The case considered is the generic one as described above (mixtures of C_3 – C_4 hydrocarbons) with $T_{inj} = 415$ K and $P_{inj} = 20$ bar. A particular fuel analysis encountered in an actual application is given in Table 6.

The mechanism follows the rules of generation described above. All possible reactions were recorded for the reactants. The processes of polymerization were stopped when C_{20} species are reached. The mechanism contains 327 species and involves 2260 reactions.

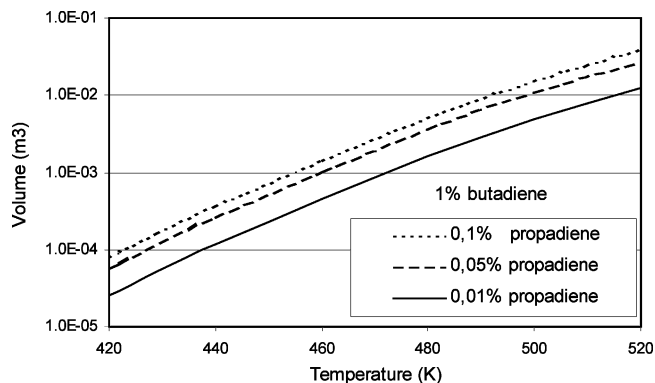


Figure 4. Volume of polymer produced in one month vs temperature and composition for a fraction of 1,3-butadiene of 1% (20 bar) and various concentrations of propadiene (propadiene). $P = 20$ bar, $\tau = 10$ s.

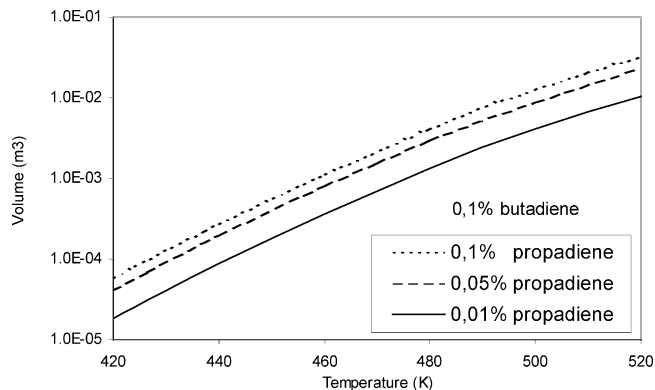


Figure 5. Volume of polymer produced in one month vs temperature and composition for a fraction of 1,3-butadiene of 0.1%. $P = 20$ bar, $\tau = 10$ s.

Table 6. Composition of the Reference Process Gas (% mol)

<i>n</i> -butane	27.1	isobutene	0.059
propene	0.019	propadiene	0.076
1-butene	45.2	1,3-butadiene	0.682
2-butene	26.9		

Since the concentration of propadiene and 1,3-butadiene are the most significant factors in the composition, the influence of their concentrations on the polymer formation has been studied starting from the composition of Table 6; the variations of concentration of unsaturated reactants in the mixture are made at the expense of the alkane. Figure 4 shows a much higher reactivity when propadiene is present as a second diolefin. However, it must be stressed that at the actual temperature of injection in gas turbines (142 °C), the depositable products are virtually undetectable even for high diolefin concentrations. However, the reaction rises exponentially with the temperature: should the temperature increase by 50 °C, then the volume of depositable products formed with 0.1% propadiene, for 5000 s and in the 50 m long pipe, would be 2.5 dm³ of polymer and several cubed meters of C_7 – C_8 as liquid. (Actually, one can show that the partial pressures of the C_7 – C_8 species formed under these conditions would still stay below the saturation.)

The influence of the 1,3-butadiene concentration is deduced from the comparison of Figures 4 (1%) and 5 (0.1%). The amount of polymer increases when multiplying the fraction of 1,3-butadiene by 10, but the effect is less dramatic than when the fraction of propadiene increases. This strong effect of propadiene is related to

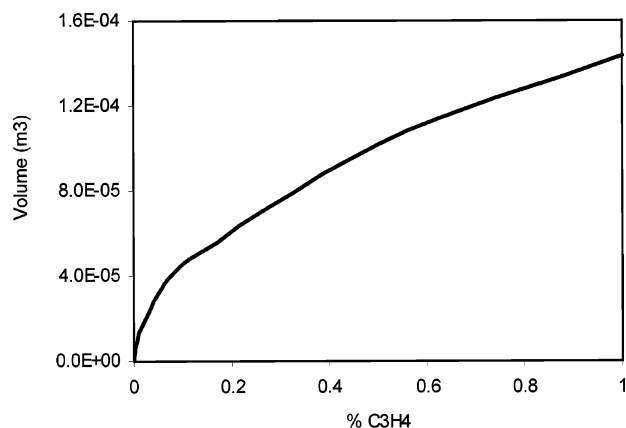
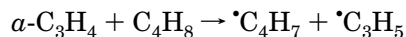


Figure 6. Volume of polymer produced in one month vs fraction of propadiene for a fraction of 1,3-butadiene of 0.68% and a temperature of 420 K. $P = 20$ bar, $\tau = 10$ s

Table 7. Volume of Polymer in 1 Month for the Different Isomers of Butene

	blend 1	blend 2	blend 3
Fraction of Olefins in the Blend			
isobutene	72.16	0	0
1-butene	0	72.16	0
2-butene	0	0	72.16
1,3-butadiene	0.675	0.675	0.675
propadiene	0.072	0.072	0.072
butane	27.1	27.1	27.1
Calculated Volume of Polymer ($T = 142$ °C)			
liquid phase (m ³)	1.2×10^{-2}	8.4×10^{-2}	6.6×10^{-3}
polymer (m ³)	5.7×10^{-5}	1.5×10^{-4}	2.2×10^{-5}

the fact that the initiation steps involving propadiene and olefins yield two resonance-stabilized radicals. For instance, in the case of 1-butene:



The activation energy is thus 23.55 kcal mol⁻¹ instead of 34.4 kcal mol⁻¹ in the case of the reaction between 1,3-butadiene and 1-butene.

While the presence of propadiene dramatically increases the quantity of polymer formed, this effect is not linear with the concentration, as shown in Figure 6. At constant temperature, the rate of polymer formation rises in a slower manner when the propadiene fraction increases.

An interesting point is the different reactivity of the three isomers of butene that are the main olefins of the mixture studied. Table 7 displays the deposits formed at 142 °C when successively considering the fraction of each isomer as the total amount of monoolefin. 2-Butene is the least reactive; isobutene produces 2 times more polymer and 1-butene nearly 7 times more. This is due to the differences in the activation energies of the initiation reactions between these olefins and propadiene. Secondary allylic H-atoms present in 1-butene are more weakly bonded and lead to much faster bimolecular initiation steps.

The effect of alkynes in the mixture has been also studied by adding 0.1% of propyne (C₃H₄) in the process

gas described in Table 6. Table 8 compares the accumulated amount of liquid phase and polymer phase for three temperatures in the cases of the reference mixture and the blended one. The addition of this small amount of propyne dramatically increases the polymerization rate. On the whole temperature range, the liquid phase remains mostly the same while the polymer phase (i.e. species containing 10–20 C-atoms in the model) grows considerably. The total amount of depositable products (liquid plus polymer) is changed only by a factor of 2, but the nature of the product is quite different, with a higher mean molecular weight.

This effect is mainly due to the easy addition of free radicals on the triple bond, as shown in the Table 3. In particular, the activation energy of the addition of the very unreactive resonance-stabilized free radicals is only 6960 cal mol⁻¹ while the addition on a diene requires 14 500 cal mol⁻¹. The higher polymerization rate results, however, from a coupling effect between diolefins and alkynes. If propyne greatly speeds up the addition of the active species, it does not influence the initiation steps that create them. The rate of the bimolecular initiations involving alkynes are similar to that of olefins. The presence of diolefins such as butadiene or propadiene will allow the fast production of the first free radicals that will further add on propyne.

The liquid phase, which results for a large part of the molecular reaction route, is not much affected by the presence of propyne. The effect of the alkynes is also a little bit less important when temperature increases, since the difference decreases between the rates of the additions.

7. Discussion

Limits of the Model. The first point lies in the definition of the polymer, which is based on the thermodynamic properties of pure substances and represents a simplified approach to the real phase equilibrium between the process gas and heavier species formed in the polymerization process.

In particular, the vapor pressure of products is not zero and thus a fraction of them remains in the gas phase. On the other hand, as a result of the classical thermodynamics of liquid/vapor equilibria, the condensing phase is not made up of only heavy molecules but is a liquid solution involving some quantities of light C₃–C₄ species, depending on the shape of the corresponding phase diagram. This “cocondensation” effect leads then to underprediction of the actual deposition rate. Accounting for such aspects of phase equilibria in extremely complex mixtures is out of the scope of this study and would require a refined thermodynamic approach and its coupling, a rather delicate task, with the kinetic modeling.

The third point relates to the concept of depositable products that lead to highly overpredicting the deposition rate. The impact of assuming a zero saturation pressure is particularly overconservative for the liquid products and can be corrected by a posteriori checks of the partial pressure. Also, the actual trend of a reaction

Table 8. Volume of Polymer Yielded in 1 Month by the Reference Process Gas (1) and a Blend with 0.1% of Propyne (2)

	142 °C		162 °C		200 °C	
	1	2	1	2	1	2
liquid phase (m ³)	5.5×10^{-2}	5.2×10^{-2}	1.9×10^{-1}	1.9×10^{-1}	2.0	2.2
polymer (m ³)	1.0×10^{-4}	8.3×10^{-2}	4.5×10^{-4}	2.3×10^{-1}	6.4×10^{-3}	1.4

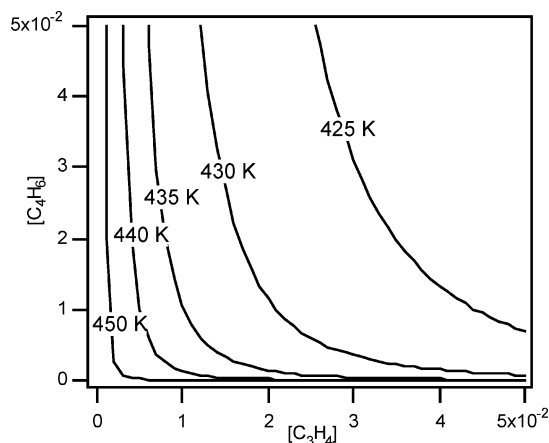


Figure 7. Isotherms of formation of 1 g/h of polymer vs mole fraction of propadiene and 1,3-butadiene.

product to deposit or not stays outside the scope of this study and may be the subject of a further experimental approach.

Fourth, the further evolution of the polymers if they condense is not taken into account. As a result of new initiation reactions, the reticulation of polymer will increase its average molecular mass, a phenomenon that is much faster in the condensed phase than in the gas phase. These reactions change the structure of the deposit but are outside the scope of this work, since they do not affect the mass and volume of deposits.

Finally, the model developed in this study considers only gas-phase reactions of hydrocarbons. The interaction of a potential catalyst has not been taken into account. In some practical cases, where deposits were observed, traces of petrochemical catalyst from upstream processes were identified as a potential driver of the polymerization in fuel circuits to the gas turbine.

Parametric Analysis. Parametric relationships relating the deposition rates to the temperature and the concentrations of butadiene and propadiene can be derived from the results of this work. One can thus express the rates of deposition of liquid and polymer in grams per hour as functions of the mole fractions of propadiene and 1,3-butadiene, with activation energies in calories:

$$m_{C_7-C_9} = 2.5 \times 10^{15} \exp\left(-\frac{20\,040}{RT}\right) X_{C_3H_4}^{1.0} X_{C_4H_6}^{0.014}$$

$$m_{\text{polymer}} = 8.0 \times 10^{14} \exp\left(-\frac{27\,000}{RT}\right) X_{C_3H_4}^{0.5} X_{C_4H_6}^{0.17}$$

Both equations are based on the previous conservative assumptions regarding deposition. The correlations are valid over the temperature range of 410–520 K, for mole fractions of each diolefin ranging between 0 and 0.05 (5%) and by keeping constant the fraction of the monoolefins at 72.4%. This kind of relationship makes it possible to draw up diagrams giving safety boundaries in terms of temperature and diolefin content. For example, Figure 7 shows the isotherms of polymer formation versus the mole fractions of propadiene and 1,3-butadiene. These isotherms correspond to a mass of depositable products of 1 g/h; on the right side of each curve, the production rate exceeds 1 g/h.

The exponential effect of the temperature is clearly visible. One can stress again the predominant effect of propadiene over 1,3-butadiene as shown by the steep

slope of the y-branches of the isotherms. Other similar diagrams can be drawn for different amounts of monoolefins.

8. Conclusions

This work was intended to break the “unpredictability myth” of the polymerization of olefins that prevailed for years in the community of gas turbines and to provide conservative guidelines, in terms of temperature and composition, for the trouble-free utilization of olefin-rich gas fuels in heavy-duty machines. The numeric approach selected to simulate the polymerization process is based on a robust mechanistic model complemented with low-temperature kinetics. This model has proven fruitful in the low-temperature/high-pressure regime of polymerization that prevails in the operation conditions of heavy-duty gas turbines. It has spotlighted the essential parts played by the temperature, the diolefins, the alkynes, and their coupling and has made possible the drawing of estimated composition diagrams.

The methodology developed in this work can be applied to other problems of gum formation in hydrocarbon that are different from the gas turbine application. More generally, the use of detailed kinetics is very helpful for many practical cases where slow minor reactions are of importance or lead to undesirable products or consequences. However, due to the numeric nature of the approach, appropriate caution must be kept when using such tools. An experimental approach could further complete the work by investigating the most critical operating conditions deduced from the model.

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