

The Impact of Saturated and Unsaturated Fuel Molecules on Diesel Combustion and Exhaust Emissions

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ABSTRACT

Diesel fuels usually comprise a wide range of compounds having different molecular structures which can affect both the fuel's physical properties and combustion characteristics. In future, as synthetic fuels from fossil and sustainable sources become increasingly available, it could be possible to control the fuel's molecular structure to achieve clean and efficient combustion.

This paper presents experimental results of combustion and emissions studies undertaken on a single cylinder diesel engine supplied with 18 different fuels each comprising a single, acyclic, non-oxygenated hydrocarbon molecule. These molecules were chosen to highlight the effect of straight carbon chain length, degree of saturation and the addition of methyl groups as branches to a straight carbon chain.

The engine tests were carried out at constant injection timing and they were repeated at constant ignition timing and at constant ignition delay, the latter being achieved through the addition to the various fuels of small quantities of ignition improver (2-ethylhexyl nitrate). In tests conducted at constant injection and constant ignition timing the ignition delay of the molecule was found to be the primary driver of combustion phasing, the balance between premixed and diffusion-controlled combustion and, thereby, exhaust emissions. However, the elimination of ignition delay as a variable, using ignition improver, revealed further, subtler, secondary combustion effects also attributable to the molecular structure of the fuels tested. For example, with constant ignition delay, the premixed burn fraction and oxides of nitrogen in the exhaust for the various fuels correlated well with the volatility and the adiabatic flame temperature.

INTRODUCTION

Future fuels will come from a diverse range of fossil and renewable sources and must be designed to ensure that combustion of liquid fuels for energy production is sustainable¹⁻⁵. In addition to the need to react to the potential dangers of climate change created by anthropogenic release of CO₂, other damaging pollutants formed during combustion, such as nitrous oxides and soot, are continuously subject to stricter controls designed to limit adverse environmental impacts⁶⁻⁸.

In the case of compression ignition engines, reductions in exhaust emissions of nitrous oxides and soot have primarily come from advances in engine technology and post combustion exhaust treatment. However, these can compromise efficiency, which is undesirable when seeking to reduce CO₂ emissions, and so design of fuels to limit pollutant emissions will become increasingly important as cleaner combustion is sought.

Present fossil-derived diesel fuels are a complex mixture of non-oxygenated hydrocarbons including alkanes, alkenes and various aromatics. Future fuels, derived from fossil and biomass sources, have the potential to be selected and processed according to molecular structure so as to best achieve a clean and efficient fuel. Of the simplest molecules suitable for combustion in compression ignition engines are non-oxygenated acyclic (no aromatic ring structures present) alkanes and alkenes.

Such molecules form the basis of fuels produced by the Fischer Tropsch process, from either biomass or fossil feedstock. Natural gas or syn-gas, obtained by the gasification of biomass or coal, is converted over a catalyst to a liquid fuel predominately composed of straight chained alkanes in the range C₂ – C₃₃, with some branched (for the purpose of this paper branched refers to addition of methyl carbon groups to

the straight carbon chain) alkanes and alcohols also present⁹⁻¹¹.

In addition to the production of alkane based fuels from biomass by biomass-to-liquid plants (BTL), other more novel routes have been observed. Wu et al. found that direct deoxy - liquefaction at 350 °C of poplar tree leaves with subsequent distillation resulted in an oil of which 34% was composed of alkanes in the range of C7 – C29¹². More exciting still is the observed potential of micro-organisms to directly produce hydrocarbons, including alkanes. Fermentation of coconuts for 9 months, under storage conditions, by the bacteria *Chrysosporum Xerophilum* was observed by Kinderlerer to produce a range of volatiles, including n-undecane, 1-nonene and 1-decene¹³. Cyanobacteria, found in microbial soil crusts in deserts are known producers of alkanes. Dembitsky et al. found one such species, *M. Vaginatus* from the Negev desert, that when grown on dry agar produced the n-alkanes octane, tetradecane, heptadecane and octadecane in addition to a variety of branched alkanes in the range of C6 - C17¹⁴. Other studies have observed cyanobacteria whose volatile production consisted of purely the four n-alkanes C8, C14, C17 and C18, with n-heptadecane by far the largest single component at 70%¹⁴.

For many years consideration of how the molecular structure of a fuel impacts on combustion phasing and emissions has been by the measurement of the cetane number of a fuel¹⁵. In addition to the many measurements of the cetane number of non-oxygenated hydrocarbons¹⁶, the cetane index utilises n – hexadecane as the baseline for a cetane number equal to 100 and 2, 2, 4, 4, 6, 8, 8-heptamethylnonane as the lower reference point with a cetane number of 15, implying that straight long chained alkanes are most suitable for diesel combustion and shorter chained, methyl branched alkanes less so.

Introduction of a double bond to a straight hydrocarbon chain has been observed to decrease the cetane number of a fuel¹⁶ both in oxygenated and un-oxygenated fuels. Schönborn et al.¹⁷, using the same experimental facility as described later in this paper, found that in fatty acid esters increasing the straight carbon chain length of the fatty acid moiety decreased the duration of ignition delay, while introduction of one or more double bonds into the fatty acid moiety increased ignition delay. Ignition Quality Tester measurements of cetane numbers of similar molecules by Knothe et al.¹⁸ also found a decrease in cetane number with increasing un-saturation, but found little impact due to the presence of branching in a molecule. In this paper fully saturated refers to molecules containing single bonds between carbon atoms, while unsaturated describes molecules containing one or more double bonds between carbon atoms.

Effects of the ignition quality on combustion phasing and emissions have been observed many times previously¹⁹⁻²¹. In general, fuels of higher cetane number produce lower NOx and higher particulate emissions. This has been attributed to changes in

ignition delay; fuels of higher cetane number, and thus shorter ignition delay, burn less of the fuel in the premixed combustion phase and thus reach lower peak heat release rates and lower maximum global temperatures. This results in lower NOx production rates^{22,23}, as NOx formation is sensitive to flame temperature. The total mass of particulates in the exhaust gas is also thermally driven and is suggested by Tree and Svenson²⁴ to be particularly sensitive to combustion phasing, based on the observations and conceptual model of diesel combustion suggested by Dec²⁵. Particles initially form in the premixed flame, but oxygen is present in sufficient quantity and temperatures are high enough for oxidation of these particles to occur. If most, or all, of the fuel is burnt during the premixed phase then total mass of particulates will be low. However, if there is a significant fraction of diffusion-controlled combustion then reduced oxygen availability means that many more soot particles will form and levels of oxidation will be lower. Furthermore, when combustion is mixing-controlled, combustion is slower and the end of combustion occurs later, with less time available for fuel oxidation prior to the opening of the exhaust valve. Therefore, it can be seen that, ignition delay is an important driver in both NOx and soot production because it influences the amount of premixed fuel and the phasing (and temperature) of combustion.

The influence of fuel molecular structure on the kinetics of ignition delay has been described by Westbrook²⁶. He highlights well the importance of low temperature kinetics (<900 K) in determining ignition delay in compression ignition engines. Autoignition occurs at a critical temperature range of between 900 – 1000 K at which accumulated H₂O₂ (hydrogen peroxide) rapidly decomposes to OH radicals. Therefore, ignition delay is a function of the rate at which this critical temperature is reached.



This is determined by the low temperature kinetic mechanisms that occur after the start of injection (SOI). As the temperature rises towards 900-1000 K, hydrogen atoms are abstracted from the fuel molecule and replaced by O₂ (Eqs. 1 & 2 and Figure 1(A); where in Eq. 2 R is the alkyl radical produced in Eq. 1 and in Eq. 2 and Figure 1(A) M is a hydrocarbon species).

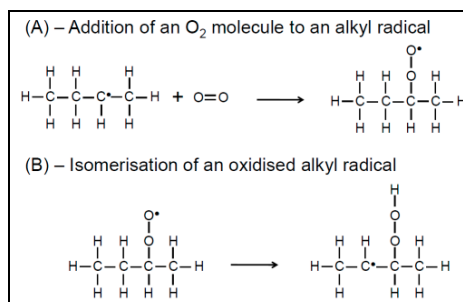


Figure 1 – Oxidation and isomerisation of a n-butane derived alkyl radical

These molecules then isomerise, with no atoms added or removed, but with the structure of the molecule rearranged (Eq. 3, in which Q is R minus one hydrogen atom, and Figure 1(B)).

Isomerisation rates are determined partly by the structure of the fuel molecule, and also the number of atoms involved (ring size). During isomerisation, a C – H bond is broken and therefore, the strength of the C – H bond is important in determining the rates of isomerisation reactions. The strongest C – H bond in an alkane chain is that of a primary carbon atom (a carbon atom with only one adjacent bonded carbon atom), followed by that of a secondary carbon atom (a carbon atom bonded to two adjacent carbon atoms) and weaker still is that of a tertiary carbon atom (a carbon atom with three adjacent and bonded carbon atoms). Following the initial isomerisation, a molecule can accept another O₂ and undergo a second isomerisation reaction (Eqs. 4 & 5, in which P is Q minus one hydrogen atom).



This molecule is then stable to around 500 K, by which point it will break down to produce at least three radical species (Eqs. 6 & 7) from the initial consumption of just one (Eq. 2).



Therefore, increasing the straight carbon chain length of a molecule and the number of weak secondary carbon to carbon bonds speeds up isomerisation reactions and the critical temperature for H₂O₂ decomposition is reached more quickly.

This paper attempts to quantify the impact on combustion and emissions of three molecular structural features: fully saturated acyclic alkanes, double bonded alkanes and branched alkanes. The paper also investigates how molecule properties other than ignition delay shape the combustion process and the exhaust emissions produced.

EXPERIMENTAL METHODS

APPARATUS

All combustion experiments presented were conducted in a single cylinder direct injection diesel engine specially designed for combustion research. Many of the fuels tested were available in only small quantities at the high assay required, or had physical properties, such as low lubricity, which would have resulted in damage to the fuel pump and common rail components. In addition, several of the fuels were solid at room temperature. So, to overcome these issues a heated, low volume and high injection pressure fuel system was designed and manufactured.

Based on the concept first proposed and implemented by Schönborn et al.²⁷, the system uses the engine common rail system as a hydraulic fluid supply so as to pressurise a small quantity of the sample fuel (100 – 250 ml) via two free pistons. The redesigned system used for the tests discussed in this paper features a bypass operated by high pressure needle valves that allows fossil diesel fuel from the engine pump circuit to flow at pressure through the test fuel circuit. This allows the fuel system and combustion chamber to be flushed with reference diesel between every test run. A schematic of the system is given in Figure 2a and an image of the fuel system installed above the engine is shown in Figure 2b. The sample fuel was supplied to the engine fuel injector via a 1 µm sintered filter element. The injector nozzle had six holes, each of 154 µm diameter. The sample fuel lines and the sample fuel pressurised system were all heated to 358 ± 2.5 K by several heating elements divided into five zones, each controlled by a separate PID controller on account of the widely differing thermal properties of each zone. Further details of the engine and control apparatus are given in Table 1.

The engine cylinder gas pressure was measured and logged at every 0.2 CAD using a piezoelectric pressure transducer (Kistler 6056AU38) and charge amplifier (Kistler 5011). At bottom-dead-centre of every combustion cycle the cylinder pressure was pegged using a piezoresistive pressure transducer (Druck PTX 7517-3257) located in the intake manifold, 160 mm upstream of the inlet valves. The normally aspirated engine had a geometric compression ratio of 15.8:1. For most tests air was aspirated into the combustion chamber at atmospheric pressure and temperature. Where fuel molecules would not combust at this condition, a PID controlled air intake heater, located 200 mm upstream of the inlet manifold, was utilised to heat the intake air to a temperature of 408 ± 2.5 K at the entrance to the inlet manifold. Various control and measurement temperatures were measured with K – type thermocouples and logged with a PC data acquisition system (National Instruments).

Exhaust gas sampling occurred 180 mm downstream of the exhaust valves to determine concentrations of gaseous species and also particulate size distribution. An automotive gas analyser system (Horiba MEXA 9100 HEGR) was used to measure the following: NO_x concentrations by chemiluminescence; CO and CO₂ concentrations with non-dispersive infrared; paramagnetic analysis to determine O₂ concentrations; and levels of un-burnt hydrocarbons were measured with a flame ionisation detector. Size and mass distributions of the sub-micron particles in the exhaust gas were determined by a differential mobility spectrometer (Cambustion DMS500). Sampling of exhaust gases for particulate measurements was made via a heated line with a dilution cyclone at the connection between the exhaust and heated line. Exhaust gases were diluted at this point by 4:1, and were diluted a second time upon entry to the analyser by 100:1. The heated line and both dilution cyclones were heated to a constant temperature of 328 K.

Engine head model	Ford Duratorq
Engine bottom end model	Ricardo Hydra
Number of cylinders	1
Cylinder bore	86 mm
Crankshaft stroke	86 mm
Swept volume	499.56 cc
Compression ratio	15.8 : 1
Maximum cylinder pressure	15 MPa
Peak motoring pressure at test conditions	3.6 MPa
Piston design	Central ω - bowl in piston
Oil temperature	353 $\pm$ 2.5 K
Water temperature	348 $\pm$ 2.5 K
Fuel injection pump	Single - cam radial - piston pump (BOSCH CP3)
High pressure fuel rail	Solenoid controlled, 160 Mpa (BOSCH CRS2)
Injectors	6 - hole solenoid controlled (DELPHI DF1 1.3)
Electronic fuel injection system	1 μ s accuracy (EMTRONIX EC-GEN 500)
Shaft encoder	0.2 CAD resolution

Table 1 – Engine specification

	Molecular formula	Assay (%)	T _{boil} (K) ²⁸	Δ vapH° (kJ/mol) ₂₈	Cetane number ¹⁶	Density (g/ml) ²⁹	Kinematic viscosity (mm ² /s) ³⁰
Reference fossil diesel	-	-	542	-	51.7	0.8345	2.672
n-heptane	C ₇ H ₁₆	99	371.5	36.66	54.4	0.6838	-
n-octane	C ₈ H ₁₈	98	398.7	41.53	64.1	0.7028	-
n-decane	C ₁₀ H ₂₂	99	447.2	51.39	76.7	0.7301	1.270
n-undecane	C ₁₁ H ₂₄	99	468	56.43	81.1	0.7402	1.602
n-dodecane	C ₁₂ H ₂₆	99	489	61.51	82.5	0.749	1.979
n-tetradecane	C ₁₄ H ₃₀	99	523	71.3	95.0	0.7627	3.050
n-pentadecane	C ₁₅ H ₃₂	99	540	76.11	96.0	0.7684	3.800
n-hexadecene	C ₁₆ H ₃₄	98	554	81.38	96.0	0.7733	-
n-octadecane	C ₁₈ H ₃₈	99	589.3	54.476 ³¹	106.3	0.7767	-
n-eicosane	C ₂₀ H ₄₂	97	616.2	-	110.0	0.7823	-
n-docosane	C ₂₂ H ₄₆	99	641.8	-	-	0.7782	-
1-octene	C ₈ H ₁₆	98	395	40.44	0.8	0.7149	-
1, 7-octadiene	C ₈ H ₁₄	97	389	32.068 ³¹	-	-	-
1-decene	C ₁₀ H ₂₀	95	440	50.44	56.5	0.7408	1.060
1-dodecene	C ₁₂ H ₂₄	95	486.2	60.78	71.2	0.7584	1.661
1-tetradecene	C ₁₄ H ₂₈	92	524.2	-	80.3	0.775	2.503
8-methyl-hexadecane	C ₁₇ H ₃₆	98	587.9 ³¹	53.048 ³¹	-	-	-
2, 6, 10, 14-tetra-methyl-pentadecane	C ₁₉ H ₄₀	98	439.2	56.336 ³¹	-	0.7827	-

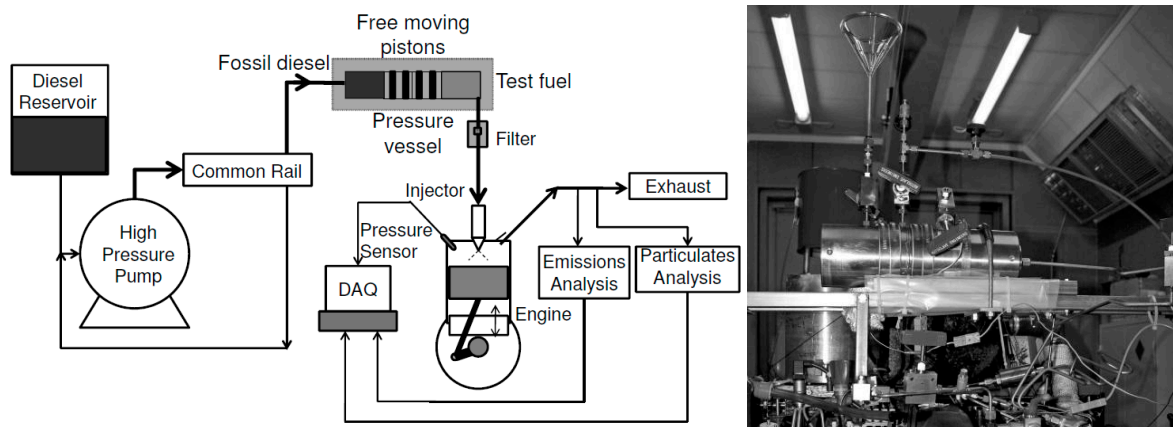
Table 2 – Fuel properties, all values of kinematic viscosity were recorded at 293 K, except that of the reference fossil diesel which was recorded at 313 K

FUEL MOLECULES INVESTIGATED

In total, 18 non-oxygenated acyclic hydrocarbons were tested so as to study the influence of three molecular structural features on combustion phasing and emissions production:

1. Straight carbon chain length.
2. Degree of saturation (i.e. No. of double bonds).
3. Carbon chain branching.

To assess the effect of increasing straight carbon chain length in a fully saturated, un-branched and non-oxygenated hydrocarbon, eleven n-alkanes were tested and were of chain length between n-heptane and n-docosane as follows: C7, C8, C10, C11, C12, C14, C15, C16, C18, C20 and C22. In order to understand the impact of a double bond within a molecule, four 1-alkenes were tested: 1-octene (C8), 1-decene (C10), 1-dodecene (C12) and 1-tetradecene (C14).



Figures 2a and 2 – Schematic and installation of the low volume fuel system

In addition one molecule featuring two double bonds, 1, 7-octadiene (C8), was included to assess the importance of the number of double bonds within a straight carbon chain. So as to study the influence of carbon branches, two molecules were specially synthesised by an organic synthesis company: 8-methylhexadecane (C17) and 2, 6, 10, 14-tetramethylpentadecane (C19). All molecules in the study, other than the synthesised branched molecules, were obtained from a chemical supplier (Sigma Aldrich UK), with assay and other properties of each presented in Table 2; the molecular structures of the fuels are given in Table 3.

A fossil derived reference diesel fuel with zero oxygen content was tested at the start and end of every day of experimentation so as to monitor drift and experimental error in the test conditions and analysis equipment. This reference diesel was also flowed through the test sample side of the fuel system and injected into the combustion cylinder between every test fuel so as to flush through any residual of the test sample and reset the injector to the same initial state for every test fuel. After flushing the low volume fuel system, the test sample fuel chamber was dismantled and cleaned thoroughly between every experiment so as to avoid cross-contamination between fuel samples.

In addition to repeat testing of the reference diesel fuel, many of the fuel molecules investigated were tested more than once at the same experimental conditions during different experiment series so as to provide another indicator of any experimental error and system drift, and also allow better overlap of data collected on different test days. The largest source of discrepancy between data collected on different days at identical conditions arose from the need to replace the injector several times during the course of the experiments. The adverse physical properties of the test fuels (e.g. low viscosity) resulted in an average continuous operational lifetime for the injectors of around 4 hours before failing shut due to port erosion within the injector body. The repeat of baseline tests with the reference fossil fuel and repeats of tests with the sample fuel enabled early detection of a deteriorating injector and its early replacement.

EXPERIMENTAL CONDITIONS

Each of the 18 molecules was initially tested at two experimental conditions: constant fuel injection timing and constant start of ignition timing. At constant injection timing the start of injection (SOI) was held constant at 7.5 CAD BTDC, at which timing the reference fossil diesel was found to combust at approximately TDC; and start of combustion (SOC) for each fuel varied according to the ignition delay of that fuel. For constant ignition timing, the SOI was varied so that the SOC of all fuels always occurred at TDC.

After the initial two sets of experiments at constant injection and constant ignition timing were completed, a third series of experiments was carried out during which the ignition delay of different sample fuels was held constant by adding the radical providing ignition improver (2 EHN) in small concentrations of up to 2.9% to each test fuel, in an iterative process to determine the correct dosage. These experiments at constant delay were conducted at both constant injection timing of 7.5 CAD and at a constant ignition time of TDC.

Where some of the test fuels were solid at room temperature, these were first melted in a PID controlled water bath held at 358 ± 2 K prior to filling of the low volume fuel system which had been preheated to 358 ± 2 K and was held at this temperature throughout the subsequent experiment.

All tests, irrespective of inlet air or fuel heating, were conducted at an engine speed of 1 200 rpm and at 45 MPa fuel injection pressure. The injection duration was adjusted between 708 – 861 μ s in the case of every fuel, so that the engine IMEP was always constant at 0.4 MPa for all fuels.

RESULTS

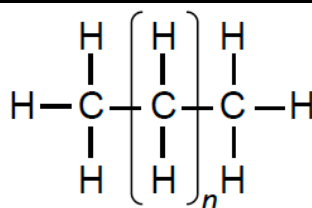
All results presented in this paper are the average of 100 combustion cycles. The standard deviation in ignition delay of each fuel is given in Table 4 and repeat measurements are shown in all plots where taken.

THE EFFECT OF INCREASING THE STRAIGHT CARBON CHAIN LENGTH OF FULLY SATURATED ALKANE MOLECULES

Results of experiments conducted at constant injection and constant ignition timing both show a strong correlation between straight carbon chain length in fully saturated alkanes and the duration of ignition delay (see Figure 3 and also Table 4 for the variance of all results). With increasing straight carbon chain length the duration of ignition delay decreases.

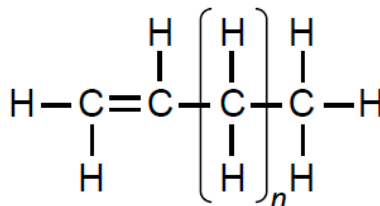
For the experimental conditions tested this impact is largest for the shortest straight chain molecules tested. For example, addition of a carbon atom to a carbon chain length of 7 has more impact on delay than addition of a carbon to a chain length of 14. Figure 3 shows that beyond C18, extension of the chain length to C20 and C22 has only a small influence on ignition delay which is not greater than the resolution of the shaft encoder of 0.2 CAD.

1. Straight carbon chain length

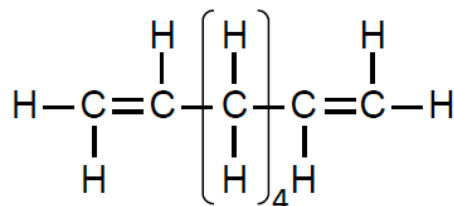


where $n = 5$ (n – heptane), 6, 8, 9, 10, 12, 13, 14, 16, 18 and 20 (n-docosane).

2. Degree of saturation

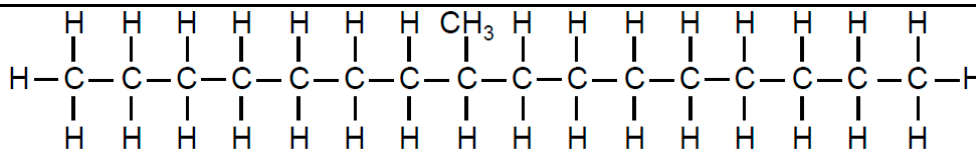


where $n = 5$ (1-octene), 7 (1-decene), 9 (1-dodecene) and 11 (1-tetradecene).

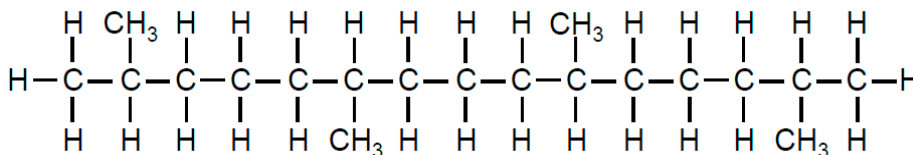


1, 7 octadiene

3. Carbon chain branching



8 methyl – hexadecane



2, 6, 10, 14 tetra-methyl – pentadecane

Where $\text{CH}_3 =$

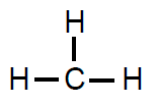


Table 3 – Fuel molecular structures



Documents

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