Cold-start hydrocarbon emissions in port-injected gasoline engines

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Abstract

An analysis is made of the sources of the high engine-out hydrocarbon (HC) emissions during cold starting of port-injected gasoline engines. A cycle-by-cycle analysis of the different parameters, which affect engine-out HC emissions, is made during the startup process. The contribution of each cylinder of a four-stroke V6, 3.3 l production engine in the total HC emissions is investigated. The HC emissions were measured in the exhaust port using a fast response flame ionization detector (FID). The effect of the initial startup position of the piston and valves in the cycle on combustion and HC emissions is examined. The mass of fuel injected, burned and emitted was calculated for each of the first 120 cycles. Different approaches to reduce engine-out and tailpipe HC emissions during cold-start are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Automotive gasoline engines; Port fuel injection; Cold-start; Combustion instability; Hydrocarbon emissions; Engine control; Exhaust treatment devices

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Nomenclature

3-W three way
ATDC after top dead center
APEHC alternator powered electrically heated catalyst
BDC bottom dead center
BO burn-off
BTDC before top dead center
CAD crank angle degrees
CVI closed valve injection
PDPA phase doppler particle analyzer
EHC electrically heated catalyst
EVC exhaust valve closing
EVO exhaust valve opening
FID flame ionization detector
FTP Federal test procedure
HC hydrocarbons
IVC inlet valve closing
IVO inlet valve opening
LA4 Los Angeles 4-mode test
LEV low emission vehicle
LIF laser induced fluorescence
LO Light-off

MAP manifold absolute pressure
MEP mean effective pressure
OVI open valve injection
PPM C3 part per million propane
REPO rapid exhaust port oxidation
SI spark ignition
SMD Sauter mean diameter
SULEV super low emission vehicle
TDC top dead center
ULEV ultra low emission vehicle

1. Introduction

Many efforts are being made to reduce air pollution originating from automotive engine emissions. Standards, developed to control the different undesirable species, are becoming more stringent requiring the reduction of engine-out emissions, as well as the use of after-treatment systems in the exhaust system. The effectiveness of these converters depends on the exhaust gas temperature, which is fairly low during cold-start. As a result, most of the tailpipe hydrocarbons (HCs) measured during the US 1975 Federal Test
Procedure (FTP 75) and ECE cycles have been found to be from the cold part of the tests, before the catalytic converter is warmed up [1–4]. These tests were conducted at normal room temperature, 21°C. At lower ambient temperatures, HCs emitted in the cold part of the test increases at a high rate [5]. A sharp peak in total engine-out HC concentration was observed right after cold-start with the engine running on three different fuels [6]. Following this peak, the HC concentration dropped and stabilized after about 20–30 s [6].

Many studies on engine-out HC emissions have been done for engines running under stable firing conditions. A comprehensive account of the HC sources and mechanisms of their formation and oxidation is given by Heywood [7] and Chen [8]. Fig. 1 shows a typical trace for the cycle resolved HC emissions averaged over 80 cycles. HCs were measured in the exhaust port of one of the cylinders, of a six-cylinder production engine, under steady state idling conditions. Fig. 1 shows that there is no spike in the HCs observed in other investigations shortly after the exhaust valve opens. This indicates that there were no HCs stored in the head quenching layer [71], and in particular the crevice volumes of the inlet and exhaust valves. The spike near the end of the exhaust stroke is attributed to the rollover eddies along the cylinder walls, being exhausted with the rest of the gases, and to the complex exhaust port flow patterns. After Exhaust Valve Closing (EVC), the HCs decreased to a nearly constant level, which is maintained throughout the remainder of the cycle.

There is a general agreement that the main sources of engine-out HC emissions in warmed-up engines running under stable firing conditions are:

1. Storage-in and release-from the crevices [7–16].
2. Adsorption and desorption of fuel vapor in the lubricating oil film [7,8,17–25].
3. Single wall quenching [7,8,26,27].

During cold-start, other sources, attributed to combustion instability, play a major part in engine-out HC emissions. Combustion instability results in partial failure, or complete failure of the flame to burn the charge. This can occur during cranking, before the first firing cycle, or even after the engine fires. Combustion instability is affected by many factors, including the quality of the air–fuel mixture, the extent of dilution with combustion products, charge temperature, engine speed and spark timing.

This article deals with the sources of engine-out HC emissions during cold-start, a detailed cycle-by-cycle analysis of the HCs emitted during cranking and the first few seconds after firing, and the different after-treatment approaches to reduce tailpipe HC emissions.

2. Typical cycles during a cold-start

Four cases are presented for combustion and the resulting engine-out HC emissions during the cold-start of a production four-stroke-cycle, V6 gasoline engine under actual running conditions. The cycle-resolved HC mole fraction is measured by a fast response Flame Ionization Detector (FID) [28]. The sample probe is located in the exhaust port of one of the cylinders, close to the exhaust valve. The cylinder gas pressure, instantaneous angular velocity, exhaust gas temperature and HC mole fraction are given in Figs. 2–5 for each case. The engine valve timing is shown on top of each figure.

2.1. Normal combustion

Fig. 2 is for a cycle where complete combustion took place. The pressure rise due to combustion started near the end of the compression stroke and peaked shortly after Top Dead Center (TDC). The instantaneous angular velocity decreased during the compression stroke of the monitored cylinder, reached a minimum at TDC, increased during the expansion stroke, and reached a peak after which it dropped due to the compression process in another cylinder. The exhaust gas temperature started to increase, shortly after the exhaust valve opened. The HC mole fraction reached
Fig. 2. A cycle with normal complete combustion.

Fig. 3. A cycle with complete but late combustion.
Fig. 4. A cycle with incomplete flame propagation.

Fig. 5. A cycle with complete misfiring.
2600 PPM C3 shortly after the exhaust valve opened, dropped to a much lower value near the middle of the exhaust stroke and started to increase near the end of the exhaust stroke. This is a typical shape of the cycle-resolved HC trace with complete flame propagation.

2.2. Late combustion

Fig. 3 is for a cycle where combustion is late. Late combustion is clear if we compare the pressure traces in Figs. 2 and 3. In Fig. 2, the pressure started to rise, due to combustion, before TDC and reached a peak value of 700 kPa at 22° of the After Top Dead Center (ATDC) in the expansion stroke. Meanwhile, in Fig. 3, there is no indication of combustion during the compression stroke. The cylinder pressure dropped at the beginning of the expansion stroke, started to rise in the expansion stroke, reached a peak at 32° ATDC, which is slightly higher than the peak compression pressure. Also, the shape of the pressure trace indicates that a large fraction of the charge burned late in the expansion stroke. Also, the instantaneous angular velocity trace indicates that the engine slowed down during the compression stroke and accelerated during the expansion stroke. This indicates that useful work was done in the expansion stroke due to combustion. It should be noted here that in such a six-cylinder engine, the instantaneous engine speed has six spikes every cycle. The two spikes after Inlet Valve Closing (IVC) are caused by combustion in the two previous cylinders.

Complete combustion is indicated from the exhaust gas temperature after Exhaust Valve Opening (EVO). Fig. 3 shows that the rise in exhaust gas temperature is more than that in the previous case where normal combustion took place. The resulting high mass-average gas temperature during the last part of the expansion stroke enhanced post-flame oxidation. This resulted in low HC emissions, i.e. 1800 PPM C3, which is lower than the previous case for normal combustion.

2.3. Incomplete combustion

In this case, the pressure rise due to combustion started very late in the expansion stroke, as can be seen in Fig. 4. The instantaneous angular velocity indicates that the engine slowed down during the compression stroke of this cycle and did not accelerate during the expansion stroke. The rise in the exhaust gas temperature was higher than in the previous two cases, indicating that combustion might have been in progress in the exhaust manifold. Incomplete flame propagation is evident from the HC mole fraction, reaching 13 000 PPM C3.

2.4. Combustion failure

Fig. 5 shows that the pressure reached its peak value before TDC, indicating the failure of combustion to start Before Top Dead Center (BTDC). Failure of combustion during the expansion stroke is evident from the pressure trace, which dropped to a fairly low value before EVO. This allows some of the gases in the exhaust manifold to flow back into the cylinder as the exhaust valve opens. Combustion failure can also be detected from the instantaneous angular velocity trace, which shows engine deceleration during the expansion stroke. The minor increase in the exhaust gas temperature, shortly after EVO, appears to be due to the flow of the hot gases from the manifold back into the cylinder. Following this rise, the exhaust gas temperature dropped during the rest of the exhaust stroke, as the cool gases were discharged from the cylinder. The drop in HCs shortly after the exhaust valve opened reflects the reduced concentration of the HCs in the gases flowing back into the cylinder. These gases are probably from the exhaust port of the cylinder itself, or from the manifold(s) of neighboring cylinders. As the piston moved in the exhaust stroke, it forced the gases out of the cylinder and the HC mole fraction reached 38 000 PPM C3.

3. Sources of cold-start hydrocarbons

Eleven sources of the high cold-start engine-out HC emissions are given in the order of their contribution. The order of the contribution of the last seven sources may vary from engine-to-engine, depending on its specific design and operating parameters:

1. Misfiring;
2. Incomplete flame propagation;
3. Wall wetting;
4. Rich fuel–air charge;
5. Crevice storage of the fuel–air charge and its release;
6. Oil dilution with liquid and fuel vapor;
7. Wall quenching;
8. Poor post-flame oxidation;
9. Exhaust valve leakage;
10. Inlet valve leakage; and
11. Lubricating oil.

3.1. Misfiring

Successful firing depends on ignition of the charge and the development of a stable flame front. Effective ignition depends on the coincidence of a flammable mixture within the spark plug gap and the occurrence of a spark. This is a tenuous process as liquid fuel is likely to be present in the gap and cause spark failure [29]. Also, spark failure may be caused by a layer of carbon and moisture deposited on the ceramic insulator allowing electrical charge leakage to ground, and hence the non-attainment of breakdown voltage [30]. Furthermore, spark failure may occur if the equivalence ratio of the charge in the gap is not within the ignition limits.

Spark failure may even happen in cycles after the first few firing cycles. Bridging the gap by condensed water vapor produced from the firing cycle may cause this. Water
condensation is enhanced during cold-start because of the cool walls.

Misfiring may occur, even after a successful electric spark, because of failure to produce a stable flame front. The stability of the flame front depends on the proper equivalence ratio of the diluted charge with residuals. For the first firing cycle during cold starting, a production engine was found to start on an in-cylinder equivalence ratio of 0.77 [31]. The engine was modified to measure the in-cylinder equivalence ratio and residual gas content of the charge during cold-start and warm-up, using a Laser Raman Scattering system. It was motored at 950 rpm, and the coolant temperature was 20°C. For cycles after first firing, a rich mixture was needed in order to compensate for charge dilution by water vapor. The range for the proper equivalence ratio was found to depend on the water vapor concentration [31], as shown in Fig. 6. Running the engine outside this range would cause misfiring. Water vapor was considered to be partially left over from the combustion products of the first firing cycle, and partially produced from water evaporated from the cool cylinder walls. Water condensation on the walls does not occur under warmed-up conditions.

### 3.2. Incomplete flame propagation

Bulk flame quenching might occur in some areas of the combustion chamber during cold-start [26,32]. Under normal steady state engine operating conditions, bulk flame quenching is not expected to contribute significantly to HC emissions. However, during cold-start transients improper spark timing, heterogeneity of the charge or high levels of residual gas may cause partial burning [8]. Partial burning and even misfiring due to dilution with residual gas may cause an increase in engine-out HC emissions even at steady loads and speeds [33]. Inward exhaust valve leakage during the intake stroke, particularly at low intake manifold pressures, may increase the residual fraction and bulk quenching [91].

### 3.3. Wall wetting

Wall wetting with liquid fuel is significant during cold starting because of the cool walls during the first few cycles of engine operation. Accordingly, overfuelling in port fuel injected gasoline engines is required to compensate for wall wetting and the poor evaporation process under cold starting conditions. Poor evaporation is caused by the heat losses to the cool walls of the intake system and cylinder during the intake process, and by the heat losses to the cool cylinder walls during the compression stroke. In addition the fresh charge is not heated by mixing with hot residual gases from the previous firing cycle. This is particularly the case in the first few cycles of the starting process, when the exhaust gas temperatures are relatively low.

The role of wall wetting in the need for delivering a fuel-rich charge in the manifold is clear if we compare the equivalence ratio needed for operation with gaseous and liquid fuels. The supply equivalence ratio for starting a single cylinder experimental gasoline engine with propane, a gaseous fuel under the test conditions, was 0.69 and independent of temperature [34]. Gasoline, on the other hand, had to vaporize to provide a combustible mixture at the spark gap before starting could occur. Fuel evaporation is strongly related to the surface to volume ratio of the liquid phase. Liquid in the form of droplets, carried with the air, has a good chance to evaporate during the compression stroke. What remains in the liquid phase at the end of compression, is expected to be the liquid wetting the walls.

Experiments on a single-cylinder engine indicated that the supply equivalence ratio needed for starting with gasoline varied from 5.6 at −29°C to 1.1 at 21°C [34]. Similar findings are reported from experiments on a multi-cylinder production engine [35]. The rich injected fuel–air charge required during the first one or two cycles of cold-start was approximately five times the amount of fuel required for a stoichiometric mixture. This initial large overfuelling is followed by underfuelling [35].

Wall wetting makes a precise control of fuel delivery very difficult during cold starting. The minimum amount of fuel needed for stable combustion in the first few cycles of cold engine start and warm-up period was investigated on a four-cylinder, four-valve, port fuel injection engine [3]. The engine was instrumented for quantitative analysis of intake port and cylinder wall-wetting, and engine-out HC emissions under firing conditions. The intake and exhaust valves were independently controlled by a hydraulic mechanism. In order to determine the amount of cylinder wall wetting, the engine was started and the valves were operated normally until the end of the exhaust stroke, where the engine was turned off with all valves closed, in order to trap the fuel inside the cylinder. Purge air at 200°C was fed into the cylinder through the spark plug hole to vaporize this trapped fuel. Finally, the vaporized fuel was analyzed by the FID and the total mass determined by integration. The cold engine was found to require much more
fuel than the warmed-up engine. It was observed that most of the fuel injected in the first cycle adhered to the intake port and cylinder wall. As the adhered fuel was carried over to the next cycle, the amount of fuel needed for the following cycle was reduced. Cylinder wall-wetting, peaked after the third cycle and gradually decreased with time. The results also showed that a large portion of engine-out HCs are emitted in the first three cycles during cold-start and decreased gradually as the engine was warmed up, a tendency similar to that of cylinder wall-wetting. This indicated that engine-out HC emissions were due to evaporation of the fuel remaining on the walls of the cylinder assembly during the expansion stroke [3]. It was also reported that the intake port wall-wetting increased until about the 300th cycle and then decreased gradually as the engine was warmed up. This was attributed to the slow increase in the port wall temperature during the first 300 cycles [3].

Liquid fuel is introduced into the cylinder in three different forms [40]:

1. **Spray droplets carried with the incoming air while the intake valve is open**: This has been shown from experiments on a four-valve port injected transparent engine. A large fraction of these droplets impinges on the cylinder wall opposite to the intake valve [41]. The engine was motored at 250 rpm to simulate cranking prior to firing. Mie scattering from the fuel droplets showed that small droplets impinge upon the cylinder wall, coalesce quickly and form a film. Similar observations were made on a quartz glass cylinder, of a four-cylinder engine [100]. Photographs indicated that in open valve injection liquid droplets of 30 μ or larger hit on the walls of the cylinder, piston and cylinder head, resulting in fuel wetting. Air-assisted injection produced better atomization and less wall wetting.

2. **Liquid fuel stripped from the intake valves and ports**: With closed valve injection most of the fuel is deposited on the back of the inlet valve. When the intake valve opens near the end of the exhaust stroke, gases at a higher pressure in the cylinder flow back into the intake port stripping the fuel from the valve and port. Part of the fuel evaporates and, together with the liquid, is carried with the air into the cylinder. This was observed in a motored engine with closed-valve injection very shortly after intake valve opening [41]. There was very little impingement of this fuel on the cylinder walls, but some fuel drops apparently impinged on the piston top. The stripped drops with closed-valve injection tend to be larger than those from open-valve injection [41]. In a fired transparent square piston engine with closed-valve injection, the liquid fuel was observed during the first few seconds of engine operation. When the engine was warmed up the fuel evaporated in the port and no liquid fuel was introduced in the cylinder [40].

3. **Liquid film squeezed and broken into droplets when the valve closes**: This was observed in a fired transparent square piston engine with closed-valve injection [40].

Wall wetting occurs in different parts of the combustion chamber and depends on the degree of fuel atomization and injection timing. Wall wetting was observed in the vicinity of the inlet valve in both Open Valve Injection (OVI) and Closed Valve Injection (CVI), in a four-valve, single cylinder research engine [36]. Laser Induced Fluorescence (LIF) and flame imaging indicated the presence of liquid films throughout the combustion chamber, including the exhaust valve. During cold starting the evaporation of the liquid film was not complete as it continued to exist even after the end of the main combustion event. In another investigation on a transparent square piston engine, droplets from the spray were detected in the cylinder near the inlet valve by using a Doppler Particle Analyzer (PDPA) [40].

Similar observations on a four-cylinder, 16-valve engine under steady state low and high load conditions indicated that under cold conditions liquid fuel entering the cylinder appeared to be the primary source of HC emissions [37].

Cylinder liner wall wetting is undesirable since some of this fuel can be trapped in the piston-liner crevice when the piston moves up [8]. Some of this trapped liquid fuel might vaporize in the crevice and flow out when the cylinder pressure decreases. The liquid fuel remaining on the liner surface might vaporize later in the expansion stroke or during the exhaust stroke, or be absorbed and desorbed by the oil layer on the liner. The crevice volume is relatively large when the engine is cold [38]. It decreases as the engine warms up because the piston temperature increases faster than the block temperature. This is due to the lower thermal capacity of the piston relative to the block. Furthermore, the aluminum piston has a higher coefficient of thermal expansion than the iron cylinder liner.

The storage of liquid fuel in the crevice during cold starting is different from the storage of a fuel–air mixture during the warmed-up operation. The vapor leaving the liquid phase in the crevice has little opportunity to mix with air and become oxidized [7,39].

The extent of cylinder wall wetting depends on the following:

1. Liquid fuel atomization;
2. Temperature of the cylinder-gases;
3. Temperature of the cylinder-wall assembly;
4. Fuel volatility; and
5. Time for liquid evaporation.

### 3.3.1. Liquid fuel atomization

Fine droplet atomization has been proven to reduce cylinder wall wetting and engine-out HC emissions. Reductions of more than 60% in HC emissions during the LA4 mode have been obtained by using a swirl type injector (Sauter Mean Diameter (SMD) = 85 mm) instead of a conventional
pintle type injector (SMD = 350 mm) [42]. Similar observations were made when an air-assisted injector was used during steady state runs [43].

Tests on a 3.0 l development engine under simulated cold-start conditions, showed that using an air-assisted fuel vaporizer allowed cold-start operation using a stoichiometric mixture without the need of enrichment [44]. This resulted in a 45–48% reduction in engine-out HC's when compared to a conventional port injection system.

3.3.2. Temperature of cylinder-gases

The cylinder gas temperature during the intake stroke is related primarily to the ambient air and residual gas temperatures. In the first few cycles of a cold-start test, the temperature of the residual gases is fairly low because of the heat losses to the cool walls. The situation is worse during the cranking cycles before the engine fires, because the residual gas may be at a temperature lower than the ambient air. In addition, during the compression stroke, the slow cranking speed allows more time for heat losses from the compressed gases to the cool cylinder walls. Accordingly, the cylinder gases reach a lower compression temperature under the low cranking speeds of a cold engine, than under the higher cranking speeds of a warmed-up engine.

3.3.3. Temperature of the cylinder-wall assembly

Evaporation of the liquid film is a function of its temperature, which is close to that of the walls. Higher liquid film temperatures result in higher partial pressures of the fuel vapor and higher mass transfer rates from the liquid to the gas phase. The increase in wall temperature after the engine fires is limited because of the high thermal inertia of the walls.

3.3.4. Fuel volatility

Fuel volatility plays an important role in liquid evaporation. More volatile fuels, having 50% lower distillation temperature, require less fuel delivery to maintain stable combustion during cold-start [3]. More volatile fuels have higher vapor pressures and molecular diffusivity at low temperatures, producing a combustible mixture with less fuel injected in the port. Less volatile fuels produce more intake port and cylinder wall-wetting and engine-out HC emissions than volatile fuels.

3.3.5. Time for liquid evaporation

The time allowed for liquid evaporation is mainly related to injection timing relative to Inlet Valve Opening (IVO). The earlier the injection before IVO, the longer is the time allowed for fuel evaporation. The timing of open and closed valve injection affects the amount of liquid transported into the cylinder [40]. With an open inlet valve, late fuel injection causes the liquid fuel to be transported into the cylinder while the charge velocities are low. This results in less evaporation and more pronounced wall wetting. With a closed valve, injecting the fuel closer to IVO allows less time for the film on the port wall to evaporate. Thus more liquid is introduced into the cylinder [40].

The effect of injection timing on droplet evaporation during the intake and compression strokes was investigated in an optically accessible cylinder, by using Laser-Induced Exciplex Fluorescence [45]. Late open valve injection, starting in the middle of the intake stroke, was found to produce droplets that did not evaporate and existed at the end of the compression stroke. Meanwhile early injection timing resulted in droplets that existed during the intake stroke but evaporated early in the compression stroke.

3.4. Rich fuel–air charge

Stoichiometric or even leaner mixtures can be used when the engine is warm. This is not the case in cold-start because of many factors:

1. The charge temperature is fairly low. 
2. Cranking speeds are low and not conducive to fuel transport and proper mixture preparation. 
3. At low speeds the compression temperature and pressure are low due to the high rates of blow-by and heat losses. In general, the engine would start and sustain combustion on leaner mixtures at higher speeds [34].
4. The engine goes through transient modes such as acceleration and deceleration.

Accordingly, rich mixtures are commonly used during cold starting because they require less ignition energy than the lean, or even, stoichiometric mixtures [7]. In addition, slightly rich mixtures have higher burning velocities than leaner mixtures [7]. This results in stable combustion and reliable operation without hesitation. Also, the range of the spark timing, in crank angle degrees (CAD) before TDC, for successful ignition and complete combustion increases with richening the mixture [34]. With all the transients during cold starting, a rich mixture produces more reliable and stable combustion over a wide range of spark timing. Rich mixtures result in higher HC emissions with different types of injectors [50], even under warmed-up conditions [11].

Rich mixture pockets may be formed in parts of the combustion chamber due to the evaporation of liquid fuel deposited on the walls during the intake stroke. Combustion of pockets of rich fuel–air mixtures were observed in the cylinder of a port fuel injected engine while the engine was running on a near stoichiometric charge [51]. The engine was equipped with a high-speed spectral infrared imaging system. In another experiment, inhomogeneities in the fuel concentration were detected near the spark plug by using an infrared fiber optic instrumented spark plug probe [95]. The inhomogeneities were strong during the intake stroke, and decreased through the compression stroke. Mixture inhomogeneities were found to increase at the end of the compression stroke when the inlet manifold was cool [52].

The oxidation of the locally fuel-rich liquid pockets was
observed to occur late in the expansion stroke causing the emission of unburned HCs. The reacting liquid layer was found over the intake valve surface when the engine was warm, and on both the intake and exhaust valves when the engine was cold. The pockets of rich fuel–air mixtures were not observed when the engine was run on gaseous fuels [51].

3.5. Crevice storage of the fuel–air charge and its release

Crevices include the piston-liner (or ring pack) crevice, valve-seat crevices, spark plug thread crevice, and cylinder head gasket crevice. The contribution of the crevice gases in HC emissions in warmed-up engines has been well documented [7,8,12–16,99]. The dominant crevice is the ring pack crevice. Overall, in a warmed engine, it is estimated that piston crevices alone contribute about 50% of the total engine-out HC emissions [37]. Unburned charge is compressed in the clearance between the piston and liner into the top land crevice during the compression and early part of the expansion stroke, before the flame arrives at the walls. In four-valve engines, where the spark plug is centrally located, the flame can be ideally considered to arrive at different circumferential parts of the wall at the same time. Accordingly most of the gases flowing into the top land crevice can be considered to have the same composition around the circumference of the ring pack. This is not the case in two-valve engines where the flame arrives at the walls at different times. The part of the top land crevice away from the spark plug contains more unburned fuel than that near the spark plug. Here the combustion products follow the unburned charge. The clearance between the piston and cylinder bore is large during starting, allowing more unburned charge to enter the top land crevice.

During the compression stroke and the early part of the expansion stroke, the high gas pressure in the top crevice forces the top ring on the lower groove flank. The radial force, due to the gas pressure on the ring back surface, in addition to the ring elastic force, seal the junction between the ring and liner. As the high pressure gases flow through the ring gap and any out-of-round clearances between the ring and cylinder, the pressure in the inter-rings crevice increases. The pressure in the inter-ring crevice depends on the balance between the flow from the top land and the flow toward the crankcase, which forms the blow-by gases. Measurements by many investigators indicated that the inter-ring pressure exceeds the top land pressure near the end of the expansion stroke [46], as illustrated in Fig. 7. This causes back flow of the gases through the ring gap and around the back of the ring when it reverses, as illustrated in Fig. 8.

As long as the top ring is forced on the lower groove flank the flow of the gases containing the unburned charge to the top land is through the ring gap and any clearance between the ring and cylinder. This is the case in the first part of the expansion stroke when the gas pressure is high. Observations using planer LIF in an operating engine, indicated that the unburned fuel escape the upper ring-land crevice, at the position of the top ring gap, during the latter part of the expansion stroke [47]. The unburned charge disperses into a thin layer along the cylinder wall. Near the end of the expansion stroke the force acting on the top ring due to the difference in pressure on its two sides, in addition to the frictional and inertial forces, may cause the top ring to reverse its position and move toward the upper flank, as illustrated in Fig. 8. This opens a large area for the inter-ring gases to flow into the top land crevice. Some of these gases, together with the charge, which is quenched in the top land, leave the crevice causing a coherent flow structure of a wall jet. Such flow was observed leaving the top land crevice opening at the ring reversal point [47]. The composition of the
gases leaving a simulated crevice in a firing Spark Ignition (SI) engine was investigated by using planar laser-induced fluorescence [48]. The gas in the ring pack crevice appeared to have a different composition than that of the fuel.

There is a general agreement that during the exhaust stroke the motion of the piston produces a roll-up vortex that mixes the HCs with the combustion products as they exit the cylinder near the end of the exhaust stroke.

During cold starting the amount of unburned fuel from the crevices during starting is much higher than that under warmed engine conditions. Results of mathematical simulations show that the piston crevice contribution to HC emissions is expected to increase during cold engine operation [38]. This increase is due to the following: (a) the higher density of the charge at lower temperatures; (b) more flame quenching near the entrance to the crevices because of the cool walls; (c) the high concentration of the HCs stored in and released from the ring pack crevice (these are a result of the large radial clearance between the piston and cylinder and the large ring gap); and (d) poor post flame oxidation, as will be explained later. Measurements showed that the mass of hydrocarbons expelled from the crevice region is proportional to the crevice volume [37], which depends on the temperature and thermal expansion of the piston and cylinder liner, as explained earlier. Experimental results confirmed that lower engine block temperature produces higher HC emissions due to higher crevice loading with the fresh charge [49]. The fuel–air charge leaving the crevice have a chance to be oxidized during the end of the expansion stroke and the exhaust stroke if the burned gas temperature is high enough. This might not be the case during cold starting.

3.6. Oil dilution with liquid and fuel vapor

The lubricating oil film is diluted with fuel vapor and liquid fuel [7,8,19–25,100]. Under warmed engine conditions, mostly fuel vapor is adsorbed in the oil film during the intake, compression and the early part of the expansion stroke before the flame arrives at the wall. Lighter fractions of the fuel may desorb and diffuse into the bulk gases during the expansion and exhaust strokes. Heavy fractions are absorbed in the oil and may reach the oil sump [53]. Oxidation of the desorbed fuel vapor may be limited by poor mixing with oxygen and low gas temperatures during cold-starting.

Dilution with liquid fuel depends on the solubility of the fuel in the lubricating oil [54]. An investigation on a research engine that can run with and without oil showed that fuels with high solubility in oil such as isooctane and iso-pentane produce significantly higher HC emissions running with oil [54]. On the other hand, fuels with low solubility in oil such as propane do not produce additional HC emissions running with oil [54]. These results confirm that fuel absorption and desorption is an important source of HC emissions and is mainly governed by the solubility of fuel in the lubricating oil [55]. Lowering the solubility by a factor of 40 leads to a HCs reduction of 30%. Absorption and desorption in the oil film increase in cold conditions [25,49,56,57].

3.7. Wall quenching

Flame quenching at the walls plays a larger role in HC emissions in a cold engine than in a warmed-up engine [58–60]. The single-wall flame quenching process is typically described by the flame quenching distance that separates the region of reactive chemistry from the region where combustion does not occur. Experiments with premixed methane air flames indicated that the flame quenching distance decreases with increasing wall temperature [61]. Under cold starting conditions HCs from wall quenching are higher than those under warmed conditions.

3.8. Post-flame oxidation

Post-flame oxidation of HCs, left over after the main combustion event, occurs in the cylinder and in the exhaust port [62–65]. If the oxidation is not complete, the fuel HCs (HCs originally present in the fuel) decreases but the non-fuel HCs increase [66]. Poor oxidation in the cylinder during the expansion and exhaust strokes and in the exhaust port results from low gas temperatures during cold-start. Experiments in a natural gas-fuelled engine [24] indicate that HC emissions are minimized by the settings of the engine operating variable which maximizes exhaust gas temperature. These settings include minimum spark advance, maximum engine load and maximum engine speed. Also, HC emissions are minimized under slightly lean operation due to the high exhaust gas temperature and increased oxygen available for post-flame oxidation.

Post-flame oxidation affects the composition of the engine-out HC emissions. Results from gas chromatography analysis [20] show that the fuel type HCs, in this case propane, represents 70–80% of the total HCs in the exhaust gases when the engine is cold, 15 s after engine start-up. However, as the engine and exhaust port are warmed-up the fuel type HCs represented only 50–70% after 120 s of engine operation. Meanwhile, the contribution of combustion products such as methane has increased to 15%, which indicates post-flame oxidation in the cylinder and/or exhaust port.

A reduction of almost 50% in HC emissions in a propane-fuelled research engine was obtained after 50 cycles of engine warm-up [21]. This reduction might have been caused by the improved post-flame oxidation. Start-up transients were not a factor because the engine was first motored at a fixed rpm by a dynamometer. Moreover, the engine was operated at a constant equivalence ratio with propane fuel, which is a gaseous fuel and has a low solubility in lubricating oil. Therefore, mixture formation, wall wetting and fuel combustion does not occur. Experiments with premixed methane air flames indicated that the flame quenching distance decreases with increasing wall temperature [61]. Under cold starting conditions HCs from wall quenching are higher than those under warmed conditions.

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absorption and desorption did not affect HC emissions. During the warm-up process the top land crevice volume decreases as the piston expands towards the liner, reducing the piston crevice volume. However, this decrease contributes only 20% to the decrease in HC emissions during engine warm-up. The remaining 80% of the decrease in HC emissions during warm-up can be attributed to the more effective oxidation in the cylinder and exhaust port caused by the higher gas temperatures [97].

3.11. Lubricating oil

The contribution of the lubricating oil in HC emissions during cold start has not been given much attention. However, as the HC emissions, originating from the fuel, are reduced to meet the stringent standards, the contribution of the lubricating oil in the total HCs will become more significant. In a recent study on a warmed-up engine the oil constituents in a hydrogen-fuelled engine were measured by a laser mass spectrometer [97]. The results showed that about 90% of the oil emitted in the exhaust gases appeared as unburned HCs. At light and medium loads, the emission of unburned oil constituents decreased with the increase in oil temperature. This has been attributed to the thinner oil film on the cylinder walls at the higher temperatures [97].

4. Cycle-by-cycle analysis of cold-start hydrocarbons

Many investigations have been conducted on single cylinder engines to study the processes, which cause the high HC emissions during cold starting. In some tests the engine was motored at constant speed by an electric dynamometer and supplied by cold air and water. Fuel was injected after the engine temperature reached its steady state value. These tests give more insight and a better understanding of many of the processes that contribute to cold-start HC emissions. However, these tests do not reproduce all the actual cold start conditions of multi-cylinder engines. The following are the differences between the conditions of single and multi-cylinder engines:

- Engine speed: In actual engines the starting process consist of five operating modes:
  1. Acceleration from stand still to the cranking speed.
  2. Motoring at the cranking speed.
  3. Acceleration upon firing in any one cylinder.
  4. Acceleration due to firing in the rest of the cylinders. One or more cylinder(s) may misfire causing instantaneous deceleration, but the engine has to accelerate to a high speed, for a successful start.
  5. Deceleration from the peak starting speed to the idling speed.

In port fuel injected engines, transients play a major role in the high engine-out HC cold starting. During deceleration the throttle valve is closed, resulting in a fast drop in the inlet Manifold Absolute Pressure (MAP). Such drop in MAP has been found to cause an increase in HC emissions not only during cold-start transients, but also during gear change with the engine warmed up [4]. The evaporation of the fuel stored on the walls of the intake manifold and port may result in a mixture too rich or too lean to completely burn. This release of fuel happens even through fuel injection is interrupted during long decelerations. After fuel flow injection is interrupted, the engine may experience fuel starvation and lean misfiring with high HC emissions for a few cycles due to wall dry-out from previous cycles with fuel injection cut-off. Also low MAP causes high dilution of the mixture by the residual gases, causing partial or even complete misfiring. It should be noted that the conditions may vary from cylinder to cylinder before the start of cranking and upon the first firing. For example, both the manifold absolute pressure and engine speed are different from cylinder to cylinder, upon the first firing cycle.

Charging process: The flow of the fresh charge into any cylinder is affected by the conditions in its intake port, which are in turn dependant on the conditions in the intake manifold, runner and main header. Meanwhile, the
conditions in the main header are influenced by the gas flow into the other cylinders.

Discharging process: Similarly, the flow of the gases out of the cylinder is affected by the pressure in the exhaust port, which in turn is affected by the pressure waves produced by the flow of the exhaust gases from the other cylinders.

Valve overlap flow: During the valve overlap period, the gas flow in and out of any cylinder is a function of the difference in the pressures in the intake and exhaust ports. These pressures depend on the valve timing of the other cylinders, in addition to engine speed.

In the following sections a detailed cycle-by-cycle analysis is made for one of the cylinders in a production multi-cylinder engine, under actual cold start conditions.

4.1. Experimental engine and procedure

A 3.3 l V6 engine was instrumented for the detailed measurement of the different operating parameters during the first few seconds of engine start-up [91]. The measurements included the cylinder gas pressure, inlet air temperature, exhaust gas temperature, inlet spark signal, fuel pulse signal, instantaneous engine speed and HC mole fraction in the exhaust port. The HCs were measured by using a high response flame ionization detector, with its probe in the exhaust port. The engine was installed in a 12′ × 12′ × 8′6′ cold room, which is a microprocessor controlled over temperatures ranging from +25°C to −10°C. A data acquisition system which 24 channels and 10 MHz sampling rate was used to record the data. The data was analyzed and a fuel inventory was made for each cycle to determine the mass of fuel injected, burned, emitted as HCs, and left over in the engine. The equivalence ratio of the mixture in the cylinder was calculated based on the mass of the fuel burned and emitted as HCs. The data presented in this section is for cylinder number 6. The firing order for the engine is 123456.

4.2. Conditions in each cylinder upon starting

At the time of starting the pistons have different positions in the cylinders. The initial position of each cylinder in the cycle upon starting is the same as that upon stopping. Observations on many four-stroke cycle engines of different types indicated that the engine is most likely to stop in a compression stroke of one of the cylinders. This is reasonable because in the expansion stroke the gases do work on the piston causing an increase in angular velocity and kinetic energy of the moving parts. The energy lost in overcoming the frictional and other losses during the exhaust and intake strokes is in general small. Most of the resistance to engine rotation occurs as the gas pressure in one of the cylinders increases during its compression stroke. Fig. 9 shows that the stopping positions in a V-6 gasoline engine was at 70 crank angle degrees before TDC in the compression stroke of one of the six cylinders. Note that for a six-cylinder four-stroke-cycle engine three compression strokes occur for each revolution. Accordingly there are three stop-positions for this engine.

Some cylinders have their inlet valves open at different positions in the intake stroke and can receive a fresh change. Other cylinders have their inlet valves closed and their positions are in either the compression or expansion strokes. Other cylinders have only their exhaust valve(s) open. Upon starting the initial pressure in all the cylinders is atmospheric, even in the cylinders where both inlet and exhaust valves are closed.

4.3. Analysis of cranking and first firing cycles

Engine cranking commonly occurs over many revolutions, depending on the ambient conditions, engine temperature and startup strategy. The data presented are for the six-cylinder engine starting at room temperature. The contribution of each of the six cylinders in the total engine-out HCs is determined.

4.3.1. Startup position is in the early part of the intake stroke

Fig. 10 shows the cylinder pressure, fuel pulse signal, electric spark signal, engine speed, MAP and cylinder-out HC mole fraction. The valve events are indicated on the top of each figure. Two cycles are shown: the first incomplete cycle, referred to as cycle 0, and the following cycle 1. The traces indicate that the initial position of the piston for cylinder 6 was at 22% of the intake stroke, while the crank was at 50 CAD after TDC. The speed trace indicates that the engine speed increased at a slow rate, as the piston of cylinder 4 was in the compression stroke, under the effect of the electric starter torque. This was followed by an increase in speed at a higher rate during the expansion stroke of cylinder 4. Cranking lasted for one and a half revolution. Cylinder 2, the first cylinder to fire, produced a sharp increase in engine speed during its expansion stroke. The inlet valve for the monitored cylinder was open and the manifold pressure was 91 kPa at inlet valve closing. The fuel delivered consisted of two pulses. The first pulse lasted for a period of 142.0 ms (103.8 CAD) and delivered 398.7 mg while the piston was in the intake stroke. The second pulse lasted for 20.2 ms (15.0 CAD) and delivered 56.7 mg while the piston was in the intake stroke. The charge in the cylinder at IVC consisted of air mixed with fuel left over from the previous run and a part of the fresh injected fuel. Under this low cranking speed, it is expected that a fairly small fraction of the injected fuel was carried with the air, and that most of the fuel was deposited on the walls of the inlet port forming a film or puddle. Evaporation of liquid under these conditions was limited because of the low air temperature and velocity, in addition to the high manifold pressure. The fuel that might have dripped into the cylinder would have been in the form of a film or large droplets deposited on the combustion chamber surfaces. The evaporation of the liquid fuel in the cylinder
was also limited. The compression pressure was 1388 kPa. The mixture formed could not burn, as indicated from the pressure trace, in spite of the occurrence of the electric spark. The HCs emitted during the exhaust stroke was 4900 PPM C3, indicating that the mixture in the cylinder had an equivalence ratio of 0.12. This is too lean to ignite.

In cycle 1 no additional fuel was injected into the port, but combustion took place, resulting in a peak pressure of 3000 kPa. The combustible mixture was formed from flash evaporated fuel in the port, fuel evaporated from the liquid film on the valve, and from the liquid fuel in any port-puddle and fuel evaporated in the cylinder. The evaporation in cycle 1 was enhanced because of the higher engine speed that reached 885 rpm at the end of the intake stroke, causing high air velocity past the film. This was in addition to the higher charge temperature at the time of ignition, which was caused by the lower heat and blow-by losses at the higher engine speed.

The major source of HCs in cycle 0 was the fuel vapor leaving the cylinder without combustion. HCs for cycle 1 are expected to be from the following sources: (a) in-cylinder wall wetting caused by the cool surfaces; (b) crevice storage and release and in particular the ring pack crevice; (c) rich fuel–air charge (equivalence ratio of 1.38); (d) oil dilution; (e) HCs desorption near the end of the expansion stroke and during the exhaust stroke; (f) wall quenching; and (g) slow post-flame oxidation in the cylinder and exhaust port caused by the low average gas temperature, in addition to the lack of oxygen in the exhaust gases. There was no indication of exhaust valve leakage.

4.3.2. Startup position is near the end of the intake stroke

Fig. 11 shows the different engine and cylinder parameters. The trace for the engine speed indicates that the engine started while cylinder number 5 was in compression. Cranking was for one and a half revolution, and cylinder number 3 was the first cylinder to fire. The traces indicate that the initial position of the piston for cylinder 6 was near the end of the intake stroke, and the crank was at 10 CAD before Bottom Dead Center (BDC) while the intake valve was still open. The fuel pulse signal indicates that the fuel was delivered in the port upon the start of cranking. This occurred while the piston in cylinder 6 was moving toward TDC in the early part of the compression stroke. The pressure in the intake manifold was 95 kPa. Probably, most of the fuel remained in the port, wetting the walls. Any fuel that reached the cylinder was likely in the form of: (a) large liquid drops, (b) stripped of the port and/or (c) squeezed between the valve and seat as the inlet valve closed [40]. The liquid fuel in the cylinder wetted the surfaces near the inlet valve [40,41], or dripped on the piston. The chances for fuel evaporation were during the compression stroke. The electric spark did not occur, and there was no combustion. The level of HCs emitted during the exhaust stroke was 4000 PPM C3, indicating that the mixture equivalence ratio was less than 0.1. It is noticed that the HCs in this case was slightly less than 4800 PPM C3 of the previous case, because the fuel had less time to evaporate.

The conditions during the following cycle produced a successful firing, as indicated from the pressure trace. The engine speed was 900 rpm at the end of compression, and MAP was 80 kPa at IVC. The fuel that was injected upon engine cranking remained in the port and had a chance to evaporate and mix with the incoming air. The equivalence ratio was 1.75. The HC mole fraction dropped from 4000 PPM C3 of cycle 0 to close to 1000 PPM C3. The mass of the HC emissions was 1.4 mg.
4.3.3. Startup position is at the middle of the compression stroke

This is the position where the engine stopped. Fig. 12 shows that compression started at atmospheric pressure and reached a peak value of 590 kPa. So the charge during the partial compression was mainly air with low HC concentration. The pressure in the cylinder dropped during the expansion stroke and reached 21 kPa at EVO. This caused a back flow of the gases from the exhaust port into the cylinder. The level of the HCs during the exhaust stroke was 1100 PPM C3. More details are given Ref. [91]. The sources of HCs in cycle 0 were mainly the gases left over from the previous run, ring pack crevice gases driven by the pressure differential between the crankcase and the cylinder near the end of the expansion stroke, and desorbed HCs from the oil film particularly during the latter part of the expansion stroke. Other source of HCs could have been leakage through the inlet valve near the end of the expansion stroke. The engine parameters and HCs left over after shut-off are discussed later in this article.

4.3.4. Startup position is in the early part of the expansion stroke

The performance of the engine in cycles 0 and 1 was
similar to that of the middle-of-the-compression-stroke position, where the cylinder pressure dropped to low values near the end of the expansion stroke.

4.3.5. Startup position is in the late part of the expansion stroke after EVO

The details of this analysis are given in Ref. [91]. Upon cranking the exhaust valve in cylinder 6 was open and the cylinder pressure was equal to the exhaust manifold pressure. The HCs from cycle 0 represented the HCs left over from the previous run. The sources of HCs for cycle 0 are similar to those of the previous case except for the lower contribution of desorbed HCs from the lubricating oil film and any leakage through the inlet valve. This is mainly due to the absence of vacuum near the end of the expansion stroke.

Fig. 11. Engine parameters for cycles 0 and 1, with initial position late in the intake stroke [91].
stroke. The sources in cycle 1 are similar to those discussed in previous firing cases.

4.3.6. **Startup position is in the late part of the exhaust stroke**

The piston was at 61% of the exhaust stroke, while the crankshaft was at 70 CAD before TDC. Fig. 13 shows the different engine parameters. The HC mole fraction in the last part of the exhaust stroke of cycle 0 was 1300 PPM C3 and represents the HCs left over in the cylinder from the previous run. The fuel delivered upon cranking consisted of two pulses. The first pulse started 50° before IVO, continued for a period of 122.0 ms (84.6 CAD) and delivered 342.6 mg. The second pulse started at 103 CAD, continued for a period of 20.0 ms (14.4 CAD) and delivered 56.2 mg. The second pulse occurred while the piston was drawing the charge in the cylinder. The cylinder misfired, despite the occurrence of an electric spark. Misfiring was mainly caused by improper mixture preparation. Most of the injected fuel impinged on the walls forming liquid films and puddles in the intake port. Also, the fuel that was carried with the incoming air through the open inlet valve probably did not evaporate and wetted the cylinder walls. The HCs emitted in cycle 1 reached 10 000 PPM C3. If we consider the fuel emitted in the exhaust to be the fuel evaporated, the
equivalence ratio in the cylinder would be less than 0.22. This is too lean for combustion. The main source of HCs was the fuel evaporated in the intake port and cylinder.

4.4. Engine parameters before and after shut-off

The HCs left over in the cylinder after shut-off might contribute to the engine-out HCs during the first cycle in the start-up process. Measurements were made on the engine for a few cycles before shut-off, and the different parameters are shown in Fig. 14. Arbitrary numbers are used to identify the cycles. Numbers on the engine speed trace indicate the cylinder that contributed in the drop in engine speed during its compression stroke and the increase in speed during its expansion stroke. The engine coasted about four revolutions after shut-off. Cycles 50 and 51 are two complete cycles where all the cylinders fired. In cycle 51 cylinders 4–6, and 1 fired. Cylinder 2 is the first cylinder that stopped firing. This is indicated from the drop in engine speed during the expansion stroke of cylinder 2. The conditions in the monitored cylinder 6 indicate that in cycle 52 fuel was delivered in the port, spark and firing occurred, and the peak pressure reached 546 kPa. HCs were around 2000 PPM C3. In cycle 53, no fuel was delivered in the
port, and neither spark nor combustion occurred. However, HCs increased to about 10 000 PPM C3. The HCs are expected to have originated from the following sources: (a) fuel evaporated from the wetted port walls, introduced into the cylinder during the intake stroke; (b) fuel desorbed from the oil film. Desorption was enhanced by the low pressure, 26 kPa, reached in the cylinder before EVO. Furthermore, the back flow of hot exhaust gases into the cylinder heated the oil film, allowing the light fuel compounds to evaporate; and (c) HCs from the ring-pack crevice, driven by the crankcase gases as they back flow into the high vacuum volume above the piston.

In cycle 54, the MAP was 37 kPa, engine speed dropped to 267 rpm, manifold pressure increased to 541 kPa, causing the compression pressure to reach 541 kPa, which was higher than the pressure reached in the previous cycle. Again, the cylinder pressure before EVO in this cycle reached a low value of 38 kPa, causing back flow of the gases in the exhaust port, which added to the concentration of HCs in the cylinder. The HCs increased by 3000 PPM C3 above the HCs in the previous cycle.

After shut-off the HCs left in the cylinders with closed valves, would condense on the walls as they cool, or be adsorbed in the oil film. The cylinders
with open inlet valves would receive some of the fuel wetting the walls of the inlet port, or would eventually release some of the HCs back into the inlet port and manifold. The cylinders with open exhaust valves would draw back some of the gases in the exhaust port as the cylinder walls cool.

Concentrations of the HCs emitted during the first cycle of the startup process depend on the amount left over from the previous run. This would vary from cylinder to cylinder depending on the conditions at shut-off.

The transient evolution of the fuel vapor phase in the cylinder, in response to a simple fuel shut-off transient, was investigated using Differential Infra-Red Absorption technique [68]. The resulting drop in the HCs concentration, at constant airflow, exhibited a characteristic delay, the duration of which depends on the volatility characteristics...
of the fuel. The delay was some 20 cycles for gasoline. Also, most of the fuel storage in the wall film was heavy ends.

4.5. Engine transients to idle speed

After cranking, the engine undergoes two transients. It accelerates to a high speed, after which it decelerates to the idle speed. Fig. 15 shows the different engine parameters for the startup position in the middle of the compression stroke of the monitored cylinder, discussed earlier in Fig. 12. The engine accelerated from 185 rpm in cycle 1 to 1443 rpm in about six revolutions; MAP dropped from 96 to 35 kPa at IVC, and the peak cylinder pressure dropped from 3012 to 614 kPa in cycle 4. The pressure and angular velocity traces indicate that combustion was stable during acceleration. HC mole fraction was 600 PPM C3 during most of the exhaust stroke of cycle 1. The increase in HCs to 2500 PPM C3 at the end of the exhaust stroke indicated the large contribution of the ring-pack crevices. The HCs during the exhaust stokes of cycles 2 and 3 kept increasing but at a slow rate. This increase might be attributed to the rise in the wall temperature, driving the light fractions of the fuel from the oil film. Similarly, there was a gradual increase in HCs at the end of the exhaust strokes in cycles 2 and 3. Cycle 4 produced HCs of 10 000 PPM C3 during the exhaust stroke and 14 000 PPM C3 at the end of the exhaust stroke. Two main factors contributed to the high HC emissions: incomplete combustion and the rich mixture. Incomplete combustion is evident from the pressure trace of cycle 4 given in Fig. 16 together with the traces for cycles 1–3. It is clear that the burn rate in cycle 4 was much slower than in the previous cycles. Note that there is no increase in pressure at TDC. This may be attributed to the drop in the density of the charge caused by the sharp drop in MAP, and to the increase in the residual gas fraction. Enriching the mixture can be attributed to the additional fuel evaporated from the wetted port walls as a result of the sharp drop in MAP, and the increase in their surface temperature.

Combustion became worse in cycle 5 where HCs reached 15 000 PPM C3 during the exhaust stroke, and 21 000 PPM...
C3 at the end of the exhaust stroke. The further drop in MAP and the increase in residual gas fraction contributed to the high HCs in this cycle. In cycle 6 the HCs was about 10,500 PPM C3 during the exhaust stroke, and reached 15,030 PPM C3 at the end of the exhaust stroke. HCs dropped in subsequent cycles until it reached a steady value in cycle 17. The gradual increase in MAP and the resulting decrease in residual gas fraction might have caused this drop in HCs.

4.6. Comparison between hydrocarbon emissions in the six startup positions

The cumulative HCs mass after the first 120 cycles for the six startup positions is shown in Fig. 17. The instantaneous mass of HCs emitted in the exhaust was calculated every crank angle degree from the mass of gases leaving the cylinder and the mole fraction measured in the exhaust port. The calculations covered the period from EVO to EVC. This was repeated for each of the 120 cycles and for each of the six startup positions explained earlier. Fig. 17 shows the relatively high contribution of the cylinder when the startup position was late in the exhaust stroke. Also, notice the high relative rate of increase of HCs during the first 10 cycles compared to the rest of the cycles. Fig. 18 gives the sum of the HCs emitted in the six starting positions, for two sets of runs. This figure is for the cumulative mass of HCs over the first 16.3 s, which is the same time taken by the engine to rotate 120 revolutions. It is clear that the trend is reproducible and the first 1.5 s contribute about one-third of the total HCs emitted during the first 16.3 s.

5. Approaches to reduce cold-start hydrocarbon emissions

To reduce the tailpipe cold-start HC emissions one or a combination of the following two approaches may be taken.

1. Reduction of engine-out HCs by basic engine design and optimized strategies to control fuel delivery, electric spark timing, and intake manifold absolute pressure.
2. After-treatment of the exhaust gases before they leave the tail-pipe.

5.1. Basic engine design and management strategies

From the above discussions, it is clear that misfiring, incomplete flame propagation, the use of a rich mixture and cylinder wall wetting are major contributors in the high cold-start engine-out HC emissions. Stabilizing the combustion process during the first few seconds of the startup process can reduce misfiring and incomplete flame propagation.

Stable combustion process requires the following:

1. Presence of an ignitable fuel-vapor–air mixture in and around the spark gap to start the flame kernel once the electric spark occurs;
2. Presence of a combustible mixture, having a proper equivalence ratio, for the flame to propagate steadily through the combustion chamber; and
3. Proper turbulence to ensure complete flame propagation with retarded spark timing.

The preparation of the ignitable and combustible mixtures depends on the design of both the fuel delivery and the air intake systems. This is in addition to the timing of fuel delivery relative to the inlet valve opening [69], as explained earlier in this article.

Controlling charge turbulence is effective in stabilizing combustion and shortening the combustion period, allowing the use of a retarded spark timing to produce high mass-average gas temperature, as illustrated in Fig. 2. This improves post flame oxidation and enhances a quick catalyst light-off. Charge turbulence depends mainly on the design...
of the intake system and ports. This can be achieved by altering valve timing and lift [70], or by controlling swirl and tumble motion [71]. Tumble flow fields are effective in shortening the combustion period by generating turbulence during the compression stroke [72]. As a result, combustion is more stable, making it possible to retard the spark without affecting combustion stability. Strong swirl flow is considered to reduce HC emissions because of the increased diffusion and oxidation of the unburned HC layer [63].

Reducing cylinder wall wetting would reduce the storage of the liquid in the ring pack crevice, dilution of the oil film with liquid fuel, and the desorption of the fuel vapor late in the expansion and exhaust strokes. Cylinder wall wetting may be reduced by optimizing the different injection design parameters and injection timing relative to the inlet valve timing. The injection parameters include the degree of atomization, spray angle and targeting relative to the inlet valve seat. For example, excessive atomization by using air-assisted injection was found not to provide significant benefits with closed valve injection [69]. Although air-assisted fuel injection did reduce HC emissions for injection on an open valve, the highest HC emissions encountered during closed valve injection without air assistance were always lower than the lowest HC emissions observed with open valve injection with vacuum air assistance [69]. Closed-valve injection was found to produce less HC emissions than open-valve injection [69]. Also, it was found that dual spray injection neither improved combustion stability nor reduced HC emissions for injection on a closed intake valve [69].

Another approach to reduce cold-start HCs is the use of a stratified charge with an overall lean fuel/air ratio. This approach was used in a 16-valve four-cylinder engine [96]. At low speeds, a strong swirl motion was produced, by partially deactivating one of the inlet valves, in order to stabilize combustion. The engine speed was monitored to detect combustion instability in any cylinder. The air–fuel ratio is monitored in each cylinder and controlled to improve combustion during the compression stroke [72]. As explained earlier, most of the HCs are emitted during the first cycle of the FTP-75 test when the catalyst is not activated due to its low temperature. The low temperature of the catalyst is caused partly by its large thermal capacity and by being placed away from the engine. This causes the exhaust gases to cool as they flow through the exhaust pipe before they reach the catalyst. For a quick warm up the converter can be close-coupled to the engine. As a result, during hot operation temperatures in the order of 100–200°C, higher than the temperatures reached in an underfloor converter [103]. This requires catalytic materials of high thermal durability to withstand temperatures in excess of 1000°C [103].

5.2. After-treatment systems to reduce cold-start tailpipe hydrocarbon emissions

Many after-treatment catalytic and absorption systems have been considered to reduce cold-start tailpipe HC emissions in order to meet the stringent ULEV and SULEV standards. The thermal oxidation reactors investigated in the early 1970s [73,74] cannot be used due to their high thermal inertia, and inability to convert nitric oxide.

The following are five types of after-treatment systems:

1. Close-coupled main catalyst;
2. Divided catalytic converter systems;
3. Heated catalysts:
   (a) electrically heated catalysts,
   (b) dielectric heated catalysts,
   (c) fuel–air charge burning systems, and
   (d) burner heated catalysts;
4. HC absorbing traps; and
5. Absorbing-catalyst systems.

The evaluation of any of these systems is based on many criteria such as their effectiveness in reducing the emissions, light-off temperature, thermal stability over extended periods and mileage, increase in back pressure, system complexity, packaging, durability, and cost. Each of the following systems has its own characteristics and advantages, and may be chosen for a certain application based on the boundary conditions.

The effectiveness of the converter is a function of its flow characteristics, catalyst carrier, catalytic coating, converter casing and the geometry of the pipes leading to the converter [94].

5.2.1. Close-coupled main catalyst

As explained earlier, most of the HCs are emitted during the first cycle of the FTP-75 test when the catalyst is not activated due to its low temperature. The low temperature of the catalyst is caused partly by its large thermal capacity and by being placed away from the engine. This causes the exhaust gases to cool as they flow through the exhaust pipe before they reach the catalyst. For a quick warm up the converter can be close-coupled to the engine. As a result, during hot operation temperatures in the order of 100–200°C, higher than the temperatures reached in an underfloor converter [103]. This requires catalytic materials of high thermal durability to withstand temperatures in excess of 1000°C [103].

A close-coupled cascade type converter with two sizes of support diameter was developed for a six-cylinder engine. A smaller diameter and shorter catalyst is followed by a larger catalyst [92]. The small entrance was found to produce more even flow distribution, and better warm-up characteristics than a one-size catalyst with a larger diameter [104]. The substrate of the first catalyst may be metallic [105] or ceramic.
Conical metallic converters, with continuously broadening channels were found to improve the flow distribution and produce more rapid light-off of the smaller cross section of the flow. Also, conical ceramic converters are being considered.

How close to the engine the catalyst can be located, depends, among other factors, on the space available in the engine compartment. The higher the catalyst effectiveness, the smaller is its volume, and the closer to the engine it can be installed. The closest the catalyst can be, is in the exhaust manifold.

The effectiveness of a catalytic converter is a function of the following:

1. geometric surface area which depends on the cell density;
2. thermal capacity which depends on the wall thickness, mass density and specific heat;
3. washcoat; and
4. precious metal type and loading.

The ratio of the geometric surface area to the thermal capacity of metal substrates is higher than that for ceramic substrates.

5.2.2. Divided catalytic converters systems

Close-coupled main catalysts are exposed to heavy thermal loads caused by the high gas temperatures reached. This was found to cause fast deterioration of the catalyst and an increase in NO\textsubscript{x}, even in the first cycle of the FTP-75 test. NO\textsubscript{x} was found to keep increasing in the following FTP test cycles, even after the catalyst was activated [75]. In addition to the heavy thermal loading, close-coupled catalysts occupy a large space in the engine compartment, which might not be available in some cars. Furthermore, due to their closeness to the engine, close-coupled catalysts may be exposed to excessive mechanical stresses caused by engine vibration.

A divided catalytic converters system, illustrated in Fig. 19, has a small-volume, low thermal inertia catalyst with metal substrate, placed close to the engine for a quick warm up [75]. The metal substrate is heat resistant and produces low back pressure. The main function of the warm-up catalyst is to oxidize the HCs until the main catalyst becomes activated. The large volume main catalyst has a ceramic substrate and runs at relatively lower operating temperatures than those of the close-coupled catalyst. Because of its large cross-sectional area it produces relatively low back pressures. Tests on such a system showed that the divided system had a higher durability and its three way catalytic conversion was better than that of the close-coupled main converter system [75]. It should be noted that, if there are no durability or space problems, a close-coupled cascade type converter would be more effective than a divided catalytic system.

5.2.3. Heated catalysts

5.2.3.1. Electrically heated catalysts Electric energy is
used to rapidly heat the light-off catalyst and achieve early effective operation in the first cycle of the FTP test.

Converters with conductive metal-based substrate containing a platinum group metal coating are used. Electric energy is supplied directly from the starter to the substrate as the vehicle is started [76]. A system using an extruded-APAHC (Alternator Powered Electrically Heated Catalyst) and thin-wall light off substrate achieved the ULEV standards without significant back pressure, even after a 100 000 mile fleet test [76].

Converters with a monolith ceramic substrate can be supplied with electric energy by using a heating element ahead of the substrate. Many investigations have been made to determine the effect of cell density and several low-power zoned heating strategies on cold-start HC emissions [77]. No difference was observed on cold-start HCs between full faced heated designs with differing geometry or thermal mass. But, hot-spot or spiral-type zoned low-power (0.75–1.0 kW) heated catalysts produced an average of 42% more cold-start hydrocarbon emissions than full-face higher-power (2.0–2.5 kW) catalysts.

A schematic of a system designed for a car powered by a 2.2 l, four-cylinder engine to meet the ULEV standard is
shown in Fig. 20 [78]. The system consisted of the following components: an EHC connected to an alternator, a secondary air system upstream of the EHC, a light-off catalyst downstream of the EHC and the main catalyst. In this system, powering the EHC by the alternator was found to be more efficient than supplying the power from the battery.

Three different cascade configurations of a monolith extruded metal powder electrically heated catalyst are schematically shown in Fig. 21 [79]. The effectiveness of each of the systems on reducing the FTP HC emissions was evaluated on a test vehicle powered by a 1.5 l engine. The results showed that the third configuration with an EHC and light-off catalyst installed near the exhaust manifold could meet the ULEV standards with secondary air injection if phase II fuel is used.

A system able to achieve rapid light-off, with emissions 40% below ULEV for a car powered by a 1.9 l engine after 50 kilo miles, is shown schematically in Fig. 22 [80]. A low thermal mass pre-converter with a typical Microlith metal catalyst substrate geometry was used upstream the ceramic main brick. A slightly rich mixture and secondary air were used, approximately for the first 40 s, for quick light-off until the engine reached closed loop operation.

5.2.3.2. Dielectric heated catalyst The use of microwave dielectric technique for rapid catalyst heating was investigated [81]. The microwave heating system in the vehicle consisted of the following components:

1. Microwave generator (magnetron and power supply);
2. Microwave transmission system, composed of line and transducer;
3. Applicator system (cavity and microwave heated catalyst);
4. Secondary air injection system;
5. Light-off catalyst; and
6. Main catalyst.

It should be noted that the use of microwave technology to heat catalytic converters is relatively new and is not well developed.

5.2.3.3. Fuel–air charge burning systems This system is referred to as Rapid Exhaust Port Oxidation (REPO) [82]. The strategy is to deliver a large amount of fuel into the engine to produce an ultra-fuel rich mixture in the cylinders and inject air into the exhaust port to produce a near stoichiometric mixture. The mixture ignites in the port and burns in the exhaust manifold and pipe leading to the catalytic converter.

This system reduced the light-off time of the catalytic converter from 45 s to less than 15 s, and reduced the HC and CO emissions by 68 and 50% respectively when compared to baseline measurements [82].

In another application a rich fuel–air mixture was used and secondary air introduced into the exhaust port near the valves in addition to electric heating of the catalytic converter [83].

5.2.3.4. Burner heated catalysts Fig. 23 is a schematic diagram of a hydrogen-burner heated catalytic converter [84]. The system consists of the following:

1. Hydrogen supply system;
2. Secondary air supply system;
3. Ignition system; and
4. Control unit.

The total HC emission level from a four-cylinder, 2.2 l engine on the FTP cycle was reduced by 46 and 62% in all FTP modes and cold transient mode respectively [84]. It is clear that this system is more complicated and expensive than the other systems.

5.2.4. Hydrocarbon adsorbing traps Zeolites and activated carbon are the most common HC trap materials used to reduce the amount of HCs emitted by a vehicle during a cold-start [85]. At start-up, when the exhaust gases are cold, HCs are absorbed by the material. As the temperature of the trap material increases as the exhaust gases get hot, the HCs are desorbed. The desorbed HCs may be oxidized by a catalyst.

The HC species trapped during the start of a 1995 vehicle with a 2.0 l engine equipped with a zeolite trap, were
identified by using an in situ mass spectrometry [85]. A sulfur-free gasoline was used. \( \text{C}_4 \), alkanes, alkenes, and aromatics were found trapped most effectively during the vehicle cold-start. Small HCs such as methane, ethane, and ethene were not trapped. It was reported that using a water trap in front of the HC trap could improve the trapping capacity of lighter molecules such as propene.

Two types of adsorbing traps were used:

5.2.4.1. **By-pass adsorption system**  Fig. 24 is a schematic of a by-pass adsorption system consisting of a first catalyst, a by-pass zeolite adsorber, a diversion valve, and a second catalyst [86].

During the first 70 s of the cold-start, exhaust gases were diverted to the hydrocarbon adsorber. The HCs were desorbed using hot gases when the engine was running at high speed and the second catalyst was warmed up at a temperature higher than the light-off temperature. Additional air was used for oxidation of the desorbed HCs. This system exhibited ULEV emissions performance on a vehicle powered by a 3.8 l, V6 engine using a fluidic flow diversion valve in the exhaust system [86]. After the first catalyst lights off, the diversion valve was shut off and the major portion of the exhaust then flows directly to the second catalyst without heating the adsorber unit.

5.2.4.2. **In-line adsorbers**  Fig. 25 shows a schematic diagram of an in-line zeolite adsorber with central hole mounted between the first and second catalysts [87–89]. In this system no valves were used. During cold-start the gases were diverted through the adsorber channels and away from the central hole by using compressed air. When the first catalyst reached its light-off temperature, the compressed air was turned off. This allowed the hot gases to pass through the central hole and heat the second catalyst. The cold-start HCs were trapped in the adsorber till the downstream catalyst was warmed up. The trapped HCs were then purged from the adsorber and oxidized by the downstream catalyst. In another configuration no secondary air was used, but purge air was supplied to the adsorber through the diverter port. This system reduced the FTP HCs to LEV standards for a 4.0 l, V8 powered car and...
to ULEV standards for a V6 3.8 l powered car. Fig. 26 shows a schematic of a system, composed of a barrel type zeolite adsorber having a central hole with two additional catalysts, all installed before the ordinary 3-W catalytic converter [90]. A Light-Off (LO) catalyst was installed upstream of the adsorber and a Burn-Off (BO) catalyst downstream of the adsorber. Secondary air could be injected before or after the LO catalyst. The LO catalyst was not active during cold-starting. It was activated during the transition stage by secondary air assistance so that the hot products of oxidation pass directly through the center hole of the adsorber to heat the BO catalyst. As the gases flowed through the adsorber, it was heated slowly due to its large thermal capacity. The slowly desorbing HCs were oxidized in the BO catalyst. In addition to its oxidation capability, the LO catalyst was utilized to further reduce NO\textsubscript{x} by the management of the air injection, in order to meet more stringent standards.

In another development an adsorber substrate, acting as a molecular sieve, was integrated into the catalytic converter [93]. The catalytically active metal was Pd-only. The sieve captures and holds the HCs, which are oxidized by the catalyst, as they are released from the sieve. Two types of HC adsorber architecture were investigated. In one approach, the adsorbing sieve, binder, and catalyst were combined in a homogeneous washcoat. In the second approach, the molecular sieve and binder are applied to the substrate first as an under layer, followed by the catalytic layer as an overcoat. Tests on a vehicle, equipped with a V8, 5 l engine, indicated that in new conditions and low mileage, levels well below the ULEV standards were achieved. The integrated HC adsorber, with a layered design showed clear aging stability under laboratory conditions, compared with the homogeneous washcoat.

5.2.5. Absorbing-catalyst system

A series flow inline system was developed in which the HCs could be stored and oxidized on the same catalized adsorber-brick, during cold starting [98]. This system can be combined with a light-off catalyst for further reduction of cold-start HCs. Adsorber systems may have secondary air injection [106], or be airless. An airless adsorber system, was developed, and consists of a first catalyst, an adsorber and a second catalyst. The system is designed to adsorb a large fraction of HCs during cold start, followed by optimized heating of the second catalyst before HC desorption. During the HC desorption cycle, the engine is running in closed loop control near the stoichiometric air–fuel ratio. The system reduced up to 38% of cold start HC emissions beyond the catalyst-only baseline, in a 3.8 l V6 vehicle, using the FTP test.

HC absorber technology is still under development and represents a cost-effective approach that can be integrated into existing exhaust systems without additional modifications [107]. When new, the absorber catalyst systems could reach HC levels below ULEV standards. Efforts are being made to improve their aging and endurance [107].

6. System optimization for low cold-start hydrocarbon emissions

A system optimization approach, including the engine and exhaust treatment devices, is needed to achieve a low tail-pipe HC emissions goal. With so many engine design and operating parameters, in addition to the after-treatment variables, it appears that each engine family might need a custom designed control strategy. For example, in engines using a rich mixture for reliable starting, engine-out HC emissions would be high, and air injection would be needed in the exhaust treatment devices. Rich mixtures would be required in engines to account for poor fuel atomization, cylinder-to-cylinder variations in air or fuel distribution, improper air motion, or poor design of the combustion chamber.

A simple system was developed to meet the ULEV standards, using only an under-floor catalytic converter [96]. The following are the main features of this system:

1. To reduce engine-out cold-start HC emissions and avoid the use of air injection in the exhaust system, a stratified charge with an overall lean mixture has been used. This
is achieved in a four-cylinder 16-valve engine by using air-assisted port fuel injection and by applying variable valve timing and lift. The swirl in the combustion chamber is increased by partially deactivating one of the intake valves.

2. To reduce the cylinder-to-cylinder variations and unstable combustion, particularly with high DI (driveability index) gasoline, the air–fuel ratio in each cylinder is monitored and controlled [101,102]. The air–fuel ratio in each cylinder is adjusted to keep the fluctuation in engine speed within a specified acceptable limit.

3. To promote quick warm up of the catalytic converter, a lined exhaust manifold connected to the catalytic converter by a two-walled exhaust pipe are used. The inside liner and tube are made of thin steel in order to reduce their thermal capacity. The air gaps between the two walls act as thermal insulators.

4. To improve the light-off characteristics of the converter, a double layered palladium catalyst is used.

5. To improve the effectiveness of the catalytic converter the cell density is increased. This is in addition to reducing the substrate wall thickness in order to reduce its thermal capacity.

7. Summary and conclusions

This article examines the factors, which contribute to the high cold-start HC emissions, and the different approaches for their control. The scope is limited to gasoline engines equipped with port fuel injection systems.

The major contributors in the high cold-start HC emissions are:

- Misfiring;
- Incomplete flame propagation;
- Cylinder-wall wetting; and
- Rich fuel–air charge.

Other contributors include:

- Crevice storage of the fuel–air charge and its release;
- Oil dilution with liquid and fuel vapor;
- Wall quenching;
- Poor post-flame oxidation;
- Exhaust valve leakage;
- Inlet valve leakage; and
- Lubricating oil.

The first few cycles of the start-up process, when combustion is unstable, are the major contributors in the high engine-out HC emissions during cold starting. Moreover, the catalytic after-treatment devices are not warmed up, allowing the engine-out HCs to appear as tail-pipe emissions.

Combustion instability, which causes misfiring even after firing, is the result of a spark failure, a lack of an ignitable mixture surrounding the spark plug gap, or a lack of a combustible mixture to carry the flame throughout the combustion chamber. Charge dilution by residual exhaust gases from a previous firing cycle may contribute to combustion failure.

The preparation of the fuel-vapor–air charge depends on the design of the injection system, the intake system and injection timing relative to the inlet valve closing. For example, more fuel atomization is not effective in reducing HC emissions with closed valve injection. Also, the earlier the fuel is injected before the inlet valve opens the better is the homogeneity of the charge.

Wall wetting during cold-start makes a precise metering of the fuel delivery very difficult. Accordingly, a rich injected-fuel–air charge is required to assure reliable starting. Moreover, wetting of the cool cylinder walls is excessive during cold-start, and contributes to the high cold-start HC emissions.

Upon starting of multi-cylinder engines, the initial conditions vary from cylinder to cylinder. Some cylinders have their valves closed, while others have either the inlet or exhaust valve open. One of the cylinders may be in the compression stroke, while another cylinder may be in the expansion stroke. These cylinders may have fuel left over from the previous run.

Tests on a V6 production engine showed that the shut down process takes about four engine revolutions after turning off the ignition key. Liquid fuel remained in the ports and cylinders.

In multi-cylinder engines the flow of gases in and out of the cylinder is affected by the conditions in the intake plenum and exhaust manifold, which in turn are influenced by the events of the other cylinders.

Approaches to reduce the high cold-start HC emissions include the optimization of the engine design and operating parameters, the use of after-treatment catalyst heating devices, or storing and burning the HCs in warmed-up catalysts. Many systems include one or a combination of the following: divided catalysts, electrically heated catalysts, burner heated catalysts and adsorbers.

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