

Shearing of Drag-Reducing Polymers with Ultrasonic Methods in Fuel-Oil Pipelines: A Feasibility Study

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ABSTRACT: The purpose of this study was to assess the feasibility and experimental conditions for the shearing of polymers (polyolefins) in fuel oil. These drag-reducing agents are mixed with fuel oil to reduce the friction during transportation in pipelines and, hence, to save energy, but they must be destroyed after use to restore all the properties of the fuel. One attractive solution consists of the use of ultrasonic energy to carry out this destruction. Ultrasound produces microbubbles (cavitation) in liquids. These bubbles grow and finally collapse, releasing a large amount of energy as a shockwave that can break polymer chains. We

studied the influence of parameters affecting cavitation on the shearing index (percentage of initial additive after sonication). We concluded that polymers A and B could be used indiscriminately. The ultrasonic energy could be injected at a frequency of 20 kHz (like in commercial equipment), and the mode of injection did not influence the yield. The results were similar in static and flowing fuels. The temperature did not exert a significant influence. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4723–4728, 2006

Key words: degradation; polyolefins; shear

INTRODUCTION

Sound–cavitation–sonochemical effects

Sound is transmitted through a medium by vibrational motions of the molecules of the medium. Sound waves above a frequency of 20 kHz are called ultrasounds.

The effects of ultrasounds on chemical reactions are not the result of any direct coupling of the sound field with the chemical species involved on a molecular level. Chemical effects are produced rather by the phenomenon of cavitation, which requires a relatively high-power density (typically between 1 and 1000 W/cm²). Sonochemistry generally uses frequencies between 20 and 40 kHz because of the availability of laboratory equipment. However, acoustic cavitation in liquids can be generated well above these frequencies. Above 5 MHz, no cavitation occurs because the acoustic energy is too weak.¹

Acoustic cavitation involves three stages: nucleation of microbubbles, bubble growth, and if the conditions are suitable, violent implosion. With the latter, a large amount of energy is released, which results in extreme

local temperatures (up to 10,000 K) and pressures (more than 1000 atm).^{1–3}

Parameters that affect sonochemistry include the frequency, solvent viscosity, solvent surface tension, solvent vapor pressure, bubbled gas, external pressure, temperature, intensity, and attenuation of sound.^{1,4,5}

Polymers and ultrasound

Ultrasonic degradation of the polymers

The complex nature of polymer molecules determines the difficulty of determining the rate equation. For dilute solutions, degradations follow first-order kinetics with rate constants being proportional to the molecular weight of the polymer.⁶

Molecules appear to break preferentially at points close to their centers.

When a macromolecule is subject to a strong mechanical action, the polymer chains not only move relative to each other but also give rise to mechanical breakages that result in active sites at the break points. The most common type of rupture is the homolytic cleavage that forms macroradicals.⁷

There is no clear agreement as to which mechanism best explains the observed effects. They have been summarized by Basedow and Ebert,⁸ who suggested that the solvent flow fields produced around cavitation bubbles serve to stretch and open out the polymer coils, which places the chain under stress. The latter is

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then broken by the shock waves caused by the final collapse of the bubbles.

Parameters influencing the ultrasonic degradation

Factors influencing the sonochemistry are interesting because they have some effects on cavitation and then affect the ultrasound degradation. Furthermore, some other observations must be noted:

- Some authors have reported that degradation is reduced at higher pressures.^{9–11}
- There are factors related to the polymer that can influence ultrasonic degradation, too:
- Some studies performed have yielded higher degradation rates at low concentrations.^{12–14}
- The degradation proceeds faster for higher molecular weights.¹⁵
- The chemical nature of the polymer seems relatively unimportant.
- It is generally accepted that degradation is more pronounced for solutions in which the polymer chain is in an extended conformation.

EXPERIMENTAL

The experiments were carried out in the frame of a European contract aimed at using polymers as drag-reducing agents (DRAs) for refined fuel transportation in pipelines.

Products

Three products were studied:

1. Additive DRA A: An active polyolefin-type substance in water emulsions.
2. Additive DRA B: An active polyolefin-type substance in gel.
3. Automotive diesel fuel for the preparation of the solutions.

Commercial confidentiality covers the exact formulation of additives.

The additives were diluted at different concentrations in fuel oil, and 800 mL of solution was always used in our experiments.

Sonochemical equipment

In all these cases, the ultimate source of ultrasound was a piezoelectric crystal. Two kinds of instruments were used to produce ultrasound.

Ultrasonic cleaning bath

The most accessible and simplest source of ultrasound was a laboratory ultrasonic cleaning bath. Generally, the ultrasonic power available in a bath with modern piezoelectric transducers is about 1–5 W/cm² with an operating frequency of approximately 40 kHz.

The amount of power obtained from the bath is low and not easily measured, can vary from bath to bath, and indeed, might even depend on the age of the bath. Furthermore, the position of the vessel in the bath is critical. Finally, control of the temperature is not easy.

A standard ultrasonic bath (Branson, model 121OE-ML; Geneva, Switzerland) with a power of 35 W for a frequency of 47 kHz was used.

Sonic horn reactor

The components of a sonic horn reactor are¹⁶

1. Generator: This is a source of alternating electrical frequency (normally 20 kHz) that powers the transducer.
2. Transducer element: The sandwich transducer element is protected by a casing, which is perforated to allow cooling.
3. Upper (fixed) horn or booster: The role of the booster is to adapt the vibration from the transducer so that it can be passed through the detachable horn at a working amplitude, which is introduced into the reactor medium.
4. Detachable horn: The detachable horn allows the vibration of the booster to be transmitted through a further length of metal, which can be used to magnify the power delivered to a system.
5. Titanium tip: Fixed on a probe, it is immersed in the sample so that an efficient transfer of energy is achieved.

The main advantages of this type of setup are that a high intensity of ultrasound is obtained.

The main disadvantages are the difficulties in controlling the temperature and the possibility of erosion of the titanium tip.

A sonic horn reactor with a high intensity ultrasonic processor (Sonics, model VCX 750; Newtown, CT) with power given until 750 W for a frequency of 20 kHz was used.

For this sonicator, the required power could not be predetermined. In fact, the ultrasonic processor was designed to deliver a constant amplitude. As the resistance to the movement of the probe increased, so did the power requirements. The power supply sensed these requirements and automatically increased the amount of delivered power to maintain the probe tip excursion at a preselected amplitude.

Thus, two parameters could be chosen and fixed: the amplitude and the time.

This processor was coupled with a data logger (Hewlett-Packard 34970A; Agilent Technologies, Inc., Palo Alto, CA) and a computer, so the delivered power could be recorded during sonication. The power was computed from the voltage measurements. Hence, the energy (in kilojoules per liter of solution) injected in solution could be calculated. Three thermocouples gave the temperatures of the box, vessel, and solution during polymer shearing.

Two probes were available: one with a tip diameter of 0.5 in. (13 mm; hereafter, the 0.5" probe) and another with a tip diameter of 1 in. (25 mm; hereafter, the 1" probe).

Working with the 0.5" probe limited the amplitude at 40% because there were some risks of tip fracture.

Another cell was also used for working in dynamic mode. This cell allowed for a maximum flow of 20 L/h. In this set up, the diesel fuel flowed by gravity. In this configuration, only the 0.5" probe could be used.

Coefficient of shearing of the polymers

The selected analytical technique was gel permeation chromatography (GPC), as it is the more appropriate technique to use when polymers are dissolved in fuels at low concentrations.

GPC is a particular case of liquid chromatography where molecules are separated as a function of their molecular size.¹⁷

A column of Plgel with particle size of 20 μm (mixed pored size), a diameter of 7.5 mm, and a length of 300 mm was selected for its ability to separate polymers of the evaluated DRAs of different molecular weights.

Although GPC does not give absolute molecular weights, relative to the reference polymers, the relative molecular weights were a good indication of the molecular weight of the polymer and its evolution in the shearing process with ultrasounds. To quantify the shearing level of the polymers in solution or mixtures, it is common to use an index that compares some property of the solution before (indicated by a subscript i) and after (indicated by a subscript f) shearing. In this case, it was defined an index called the shearing index (SI):

$$SI = 100 \times \left(\frac{M_{wi} - M_{wf}}{M_{wi}} \right) \quad (1)$$

where M_w is the average molecular weight

In comparing the SI and the energy injected in solution, we could calculate the efficiency.

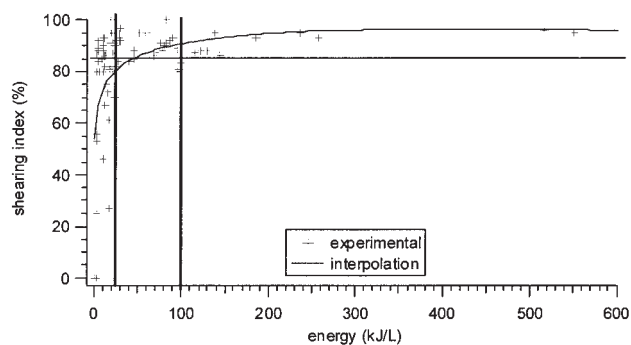


Figure 1 SI of the solutions of DRA A dissolved in fuel oil and treated with ultrasound.

RESULTS AND DISCUSSION

Introduction

The presented set of results enabled us to obtain a series of tendencies concerning the efficiency of the shearing additives by sonication.

Around 100 samples were used, and the following properties were varied:

1. Type of additive (DRA A and B).
2. Frequency of ultrasound (bath at 47 kHz and probes at 20 kHz).
3. Temperature (5–50°C).
4. Power (10–270 W) and energy flow rate (5–30 min).
5. Concentration of DRA in the fuel oil (5–200 ppm).
6. Sonication setup (static or dynamic).
7. Probe type (1" and 0.5").
8. Used energy (0–250 kJ/L).

Results and discussion

Because the drag-reducing polymers were two polyolefins and because they are used in small concentrations in fuel oil, they would not have influenced the property of solvent significantly in a different way (like vapor pressure). It was logical, then, that in all experiments, no significant difference was observed between the behavior of the two additives (DRA A and B).

All the results obtained for the DRA A polymer are shown in Figure 1.

Figure 2 gives all the results obtained for the DRA B polymer.

The scattering on these graphs is important because all experiments are shown here, whatever the parameters of sonication. Nevertheless, as shown, the coefficient of shearing (of DRA A and B) did not improve for energies greater than 100 kJ/L. In good conditions, 25 kJ/L was enough to give good results; this meant a

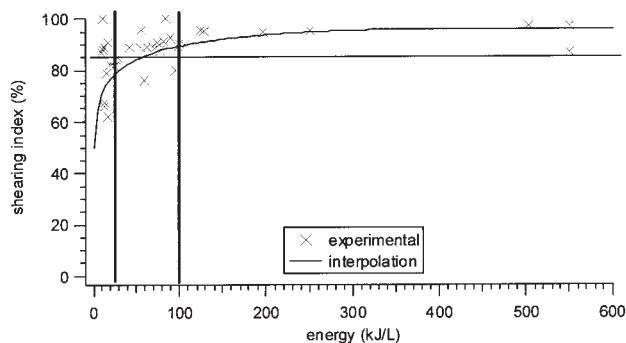


Figure 2 SI of the solutions of DRA B dissolved in fuel oil and treated with ultrasound.

shear of more than 85% of the drag-reducing polymers.

To influence the frequency, solutions of DRA A at 48 ppm and DRA B at 44 ppm were prepared. An ultrasonic bath (ultrasound frequency = 47 kHz) or a sonic horn reactor (ultrasound frequency = 20 kHz) were used to shear polymers in these solutions with energies between 10 and 200 kJ/L.

With the 1" probe, the efficiency of ultrasound to shear 62% of polymers was 3.5% L/kJ. To obtain SIs greater than 85% with the ultrasonic bath and the 1" probe, the efficiencies were 0.6 and $1.7 \pm 0.2\%$ L/kJ, respectively.

The ultrasonic bath had a lower efficiency than the probe and will not be used in further experiments. Lower frequencies of ultrasound seemed to give better results for the shearing of the additives, but beyond 100 kJ/L, the influence of the frequency was very small.

The temperature naturally increased during sonication because of energy releases. To limit temperature increases, water baths were used. When temperatures were too high, the sonication was stopped, and the solution was cooled before the sonication started again. The nominal temperatures were the average during the whole shearing process. Samples of DRA B with a concentration of 40 ppm were processed with the 1" probe. Two samples were cooled to -3°C , and the average temperature was $20\text{--}30^{\circ}\text{C}$. Two other samples with average temperatures of 40 and 50°C were processed but with higher energies (60 and 550 kJ/L, respectively). The SI was 87% with a standard deviation of 5%.

No significant temperature effect on SI was observed in our range of work (between 5 and 30°C). For the temperatures of 40 and 50°C , we could not affirm that there was not any effect of temperature because the energies used were higher.

A sonic horn reactor with 0.5" and 1" probes was used to degrade the DRA polymers with energies between 5 and 520 kJ/L to determine the influence of

the instantaneous power. In the following results, the concentration of DRA A was 48 ppm or 200 ppm, and for DRA B, it was 200 ppm. With the 1" probe, the efficiency of ultrasound for a concentration of 200 ppm and powers of 36, 44, 234, and 239 W to obtain 90% shearing was $1.2 \pm 0.1\%$ L/kJ. With the 0.5" probe, the efficiency of ultrasound for a concentration of 48 ppm and powers of 11 and 35 W to obtain 85% shearing was $3.3 \pm 0.3\%$ L/kJ.

The values of the power showed no significant differences in the efficiency. The energy flow rate had no effect on the efficiency. This meant that there was no reciprocity effect and that the ultrasonic power could be applied at a chosen rate without influencing the result.

Solutions with different DRA concentrations in fuel oil were prepared for the two polymers from 5 to 200 ppm. The sonic horn reactor with the 1" probe was used. In the experiments reported in Figure 3, the temperature of the solution was maintained around 30°C , the energy was about 18.5 or 87.5 kJ/L, and the power was about 52 or 247 W.

As we waited, it seemed that the smaller the concentration was, the better the percentage of shearing was. However, good shearing coefficients were obtained up to 200 ppm when sufficient energy was injected. Experimentally, a minimum of SI was obtained between 50 and 200 ppm DRA. The lower concentrations were studied more because they are used in practice in pipelines.

Solutions of 48 ppm DRA A and 47 ppm DRA B were processed by ultrasound in the two modes (static

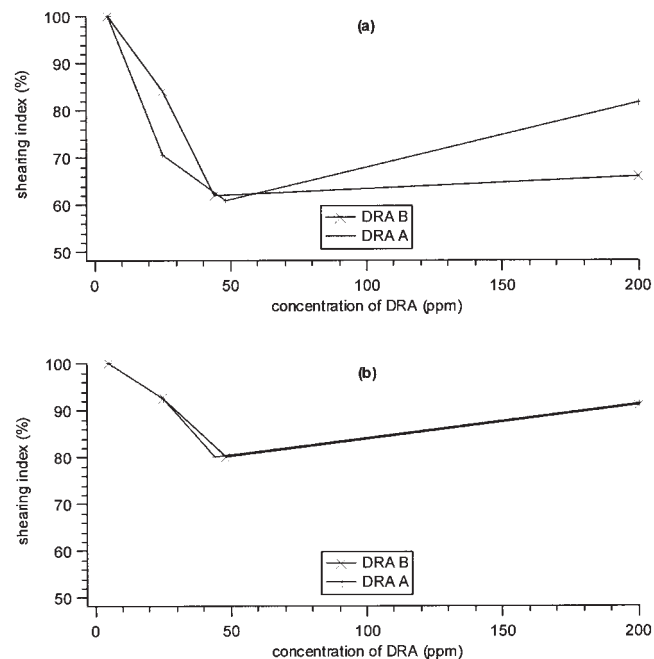


Figure 3 SI of solutions of DRA A and DRA B dissolved in fuel oil and treated with a sonic horn and the 1" probe at an energies of (a) 20 and (b) 87 kJ/L, respectively.

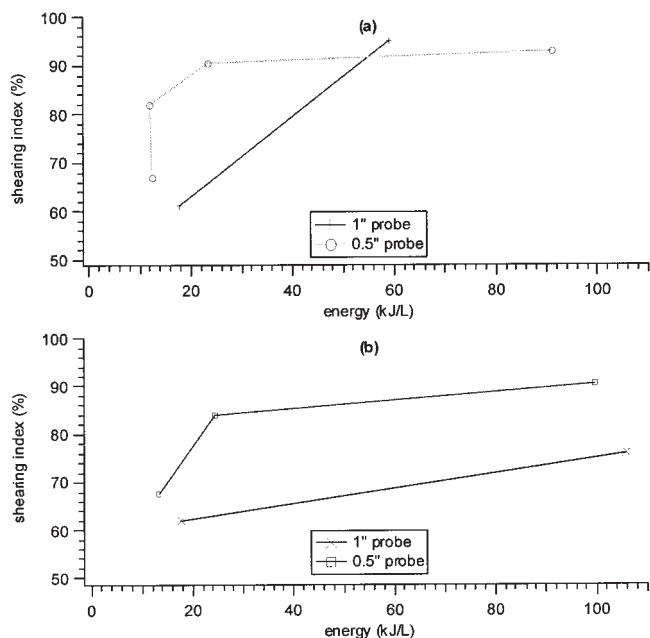


Figure 4 SI of solutions of (a) DRA A at 48 ppm and (b) DRA B at 47 ppm in fuel oil and treated with a sonic horn at about 30°C.

or dynamic). The 0.5" probe was chosen because it could be adapted to the flow cell where the solution was passing. For the two polymers, the maximal amplitude of vibration, which was limited for technical reasons at 40%, was chosen. The realization of a dynamic mode in the laboratory was more complicated, and the reproducibility in these conditions was more delicate. Then, at low energy, where the SI slope was important, the lowest perturbation of a parameter had the largest influence on the SI. The sonications with static or dynamic arrangements gave the same results (e.g., see Fig. 5, shown later).

A sonic horn reactor with a 0.5" or 1" probe was used to degrade the two additives with energies between 10 and 105 kJ/L to determine the influence of the horn size. In the two following graphs, the concentration of DRA A was 48 ppm, and that of DRA B was 47 ppm. To shear about 65% of the 48-ppm solution of DRA, the efficiency of the 1" and 0.5" probes were, respectively, 3.5 and $5.2 \pm 0.2\%$ L/kJ. With the 0.5" probe, to obtain a SI greater than 85%, the efficiency of the ultrasound had to be $3.7 \pm 0.2\%$ L/kJ.

The 0.5" probe gave a better efficiency than the 1" probe (see Fig. 4). This probe was considered to be best fitted to the size of the reaction vessels.

A sonic horn reactor with a 0.5" probe was used to degrade DRA polymers with energies between 10 and 250 kJ/L to determine the minimum energy useful to shear 80% of the polymers. In the following graphs, the concentration of DRA A was 48 ppm, and that of DRA B was 47 ppm.

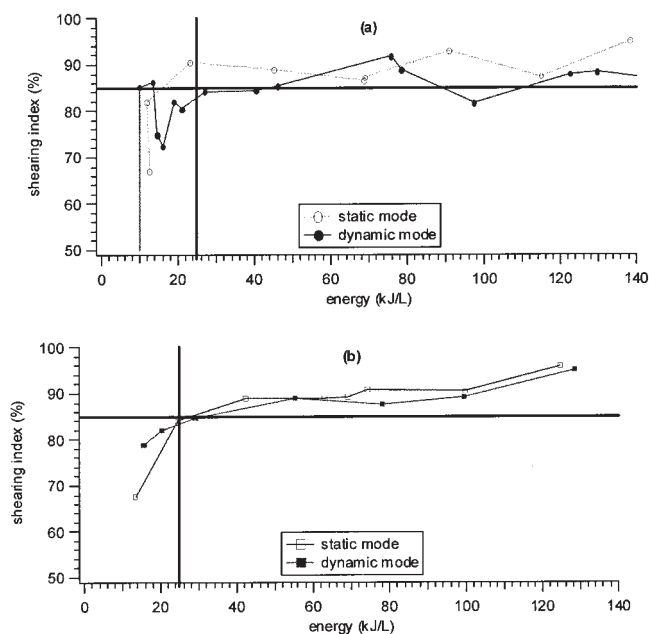


Figure 5 SI of solutions of (a) DRA A at 48 ppm and (b) DRA B at 47 ppm in fuel oil and treated with a sonic horn and the 0.5" probe in the static and dynamic setups.

The energies used to shear 80% of the initial additive were, respectively, about 20 and 50 kJ/L of solution with the 0.5" and 1" probes.

All figures show that above 85% shearing, there were some saturation effects.

The realization of a dynamic mode in the laboratory was more complicated, and the reproducibility of the operations was more delicate. Between 10 and 25 kJ/L, the SI slope was important. Then, the lowest perturbation of a parameter had the largest influence on SI. This explains the scattering in Figure 5.

For concentrations lower than 30 ppm, the efficiency of the 0.5" probe was $16.8 \pm 0.4\%$ L/kJ (see Fig. 6).

With a concentration of 10 ppm and the 0.5" probe, the kinetics were studied. The kinetics are usually shown by an exponential function of time. Under these conditions, the power injected by ultrasound to

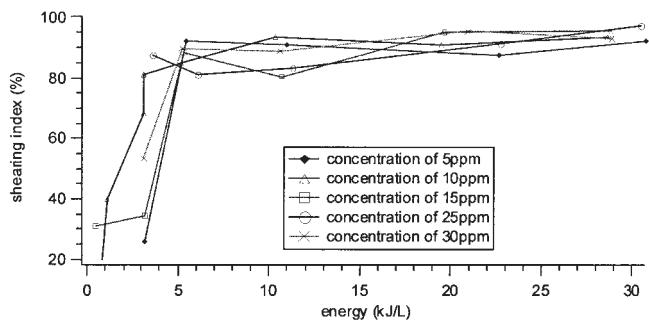


Figure 6 SI of solutions of DRA A in fuel oil and treated with a sonic horn and the 0.5" probe.

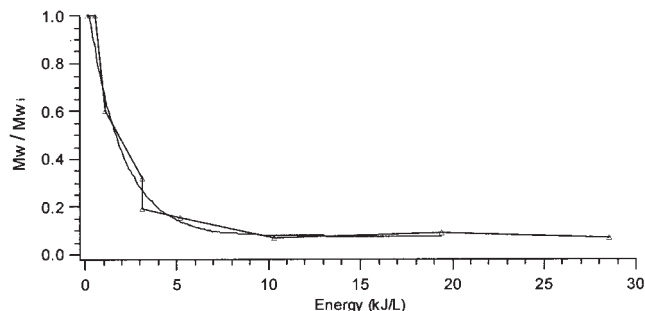


Figure 7 Kinetics of the degradation of DRA A (solution at 10 ppm) with the 0.5" probe by ultrasound.

the solution should have been constant. However, with our installation, the power could not be fixed. Thus, a more significant way to express kinetics was to write it in a function of the energy put in solution by the ultrasonic wave (E ; see Fig. 7).

$$\frac{M_w}{M_{wi}} = A \times \exp(-kE) \quad (2)$$

where A and k are constants with the values: $A = 1.05 \pm 0.05$ and $k = 0.45 \text{ L/kJ} \pm 0.05$.

CONCLUSIONS

1. Two DRAs, DRA A and DRA B, were tested. No differences in shearing under acoustic energy were found between these two polyolefins.
2. Between 20 and 47 kHz, 20 kHz gave better SI results. With the available sonication equipment, the frequency was generally fixed around 20 kHz, and field equipment with a tuneable frequency is difficult to find. This frequency was used with a good efficiency for all experiments.
3. The effect of the temperature on shearing efficiency was not evident between 5 and 30°C. Maybe the high temperature (>40°C) had a bad influence on the shearing by ultrasound.
4. For a given energy applied to the fuel, the ultrasonic energy density had no significant influence. This means that the application of the

ultrasonic energy at a high rate during a short time, or with a small rate during a longer time, led to similar results. The same results were obtained if the total needed energy was applied in one or several steps. This finding will enable the ultrasonic zones to be displayed along the pipeline if necessary.

5. The comparison between shearing in the static and dynamic modes showed no significant differences. This finding shows that the results in the laboratory beakers are applicable to flowing fuels if the design is adapted to the size of pipelines.
6. The SI was higher when the initial additive concentrations were low.
7. From the average of all tests, to obtain a SI of 85% and with a concentration of about 50 ppm DRA, the efficiency of the ultrasonic bath and 1" and 0.5" probes were, respectively, 0.6, 1.7, and 3.5% L/kJ. For concentrations lower than 30 ppm, the efficiency of the 0.5" probe increased to $16.8 \pm 0.4\% \text{ L/kJ}$.

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