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EXPERIMENTAL INVESTIGATION OF THE TEMPORAL AND RADIAL VARIATION OF THE COMPOSITION OF WAX DEPOSITS FORMED IN AN ANNULAR TEST SECTION

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Abstract. *Wax deposition in subsea oil production and transportation pipelines is a relevant problem for the industry. For decades, efforts to build models capable of predicting the phenomenon have been carried out in order to minimize significant production losses, as well as costs for the removal of wax deposits that may form on the internal surface of the pipes. When the oil from the reservoir is cooled below a critical temperature, wax crystals precipitate leading to the formation of deposits that, later, are enriched of heavier paraffin fractions. This critical temperature is called WAT – Wax Appearance Temperature. In the present work, controlled experiments were carried out in a laboratory scale test section with a test solution consisting of 20% paraffin, and 80% solvent, and a WAT of 35.6°C, to investigate the deposit aging effect for different cold wall temperatures, cooling rates, and Reynolds numbers. The experiments durations ranged from one to seven hours. A deposit sampling port allowed rapid removal of the deposits avoiding significant changes in the deposit composition during the sampling. The two cold wall temperatures investigated (WAT-23.6°C and WAT-12.6°C) showed that the composition differences only begin to be significant approximately two hours after the deposit has reached its final thickness. The three Reynolds numbers investigated presented a small influence on the deposit composition. In addition, for one of the cold wall temperatures, at the high cooling rate, the radial concentration of the deposits was investigated by using a device to slice the samples precisely in half. It was found that the part closer to the hot flowing oil was enriched in heavier carbons, while the half closer to the cold wall did not present significant changes with time.*

Keywords*: Wax deposition, Wax composition, Deposit slicing, Deposit aging, Molecular diffusion*

1. INTRODUCTION

Wax deposition has been the focus of research for many years due to the relevant problems caused in the oil production and transportation, especially in subsea pipelines (Chala et al., 2018; Liu et al., 2021; Yu et al., 2021; Fan, Li and Li 2021). Wax deposits progressively build on the pipe inner wall leading to decreased oil production, increased pumping power and, in critical situations, to the loss of the pipeline installation. (Akinyemi et al., 2018; Singh et al., 2000; Gluyas and Underhill, 2003).

The deposits are known to be formed by a porous crystalline matrix filled with liquid wax. In addition, the structure of the deposit changes with time, becoming richer in high molecular weight molecules and with smaller amounts of liquid. In general, molecular diffusion and shear effects were cited in the literature as the main mechanisms that would produce enrichment of heavier fractions, the so-called aging effect (Singh et al., 2001; Mahir et al., 2018; Fan et al., 2022).

Predicting the composition and mechanical characteristics of the wax deposit is relevant to understand the growth and aging process of the wax deposit. Furthermore, knowing the characteristics of the wax deposit composition, it is possible to provide insights into the methodology for removing wax deposits from the pipeline walls (Liu et al., 2021; Yu et al., 2021); Fan, Li and Li, 2021; Zheng et al., 2017).

Singh et al. (2001b) proposed that the aging process is directly related to the temperature gradient across the deposit, suggesting that when the temperature gradient approaches zero, the aging process ceases. More specifically, the work by Singh et al. (2001b) suggests that a certain carbon number indicates the limit for the counter diffusion process. This means that molecules with carbon numbers greater than this critical value diffuse into the deposit and those below that value diffuse out. The result of this process would be the variation in the carbon distribution of the deposit when subjected to a long deposition process (Quan et al., 2015; Fan, Li and Li; 2022).

Fan, Li and Li (2022) found that the wax content was not evenly distributed inside the deposit. The authors observed that the wax concentration was higher closer to the deposit interface, and that it decreased as it approached the cold surface. The deposit aging effect was responsible for reducing this difference in concentrations between the layers of the deposit.

In the present work, a series of composition experiments were carried out with the objective of extracting experimental information about the temporal and spatial variation (radial direction) of the composition of the deposit that can provide a useful database for the development of more detailed wax deposition models. Wax composition was obtained as a function of time, providing fundamental information to develop and validate the predictions of deposition models. The experimental data obtained in this work are currently being used validate detailed compositional models under development in our laboratory, but no presented in the present work.

2. EXPERIMENTAL SET-UP

The experiments were conducted in a flow loop type test section schematically illustrated in Figure 1. The deposition experiments were performed in the annular section indicated at the bottom of the figure. This test section consisted of an annular assembly formed by a copper pipe mounted concentrically to an acrylic pipe, through which the wax solution was pumped. This annular section was placed inside a tank filled with water at a controlled temperature of 38°C, which corresponded to the same inlet temperature of the test solution in the section. The careful control of the testing conditions was essential to obtain reliable results that could later be used to validate numerical simulations. Two thermostatic baths were used to control the temperature of the deposition surface. One bath was set at a hot temperature of 38 °C, while the other at a colder temperature of 12 °C. A volumetric pump was responsible for pumping the wax solution at a constant flow rate through the annular section after passing by a filter positioned at its entrance.

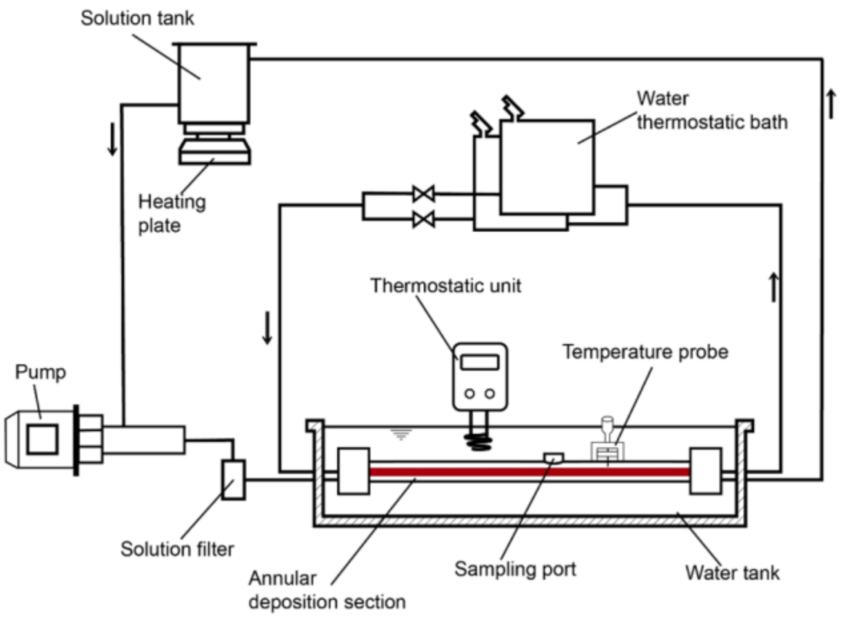

Figure 1. Schematic view of the test section employed in the wax deposition studies. Figure from Veiga et al. (2020)

The test solution located in the reservoir was heated by a heating plate and was under constant agitation for keeping it homogenized. In addition, heating tapes were installed surrounding the reservoir to assist in the solution melting as well as around the flow lines to avoid unwanted wax precipitation. This temperature system was controlled with a proportionalintegral-derivative-controller (PID) in order to maintain a constant temperature of the solution at the inlet of the annular assembly. The test solution used in this experiment consisted of 20% paraffin, with carbon numbers ranging from C_{22} to C_{39}, and 80% solvent, which in this case was dodecane, C_{12}. One of the great advantages of this test solution is that it has a clear distinction between the paraffinic components and the solvent, as can be seen in the chromatogram of Figure 2.

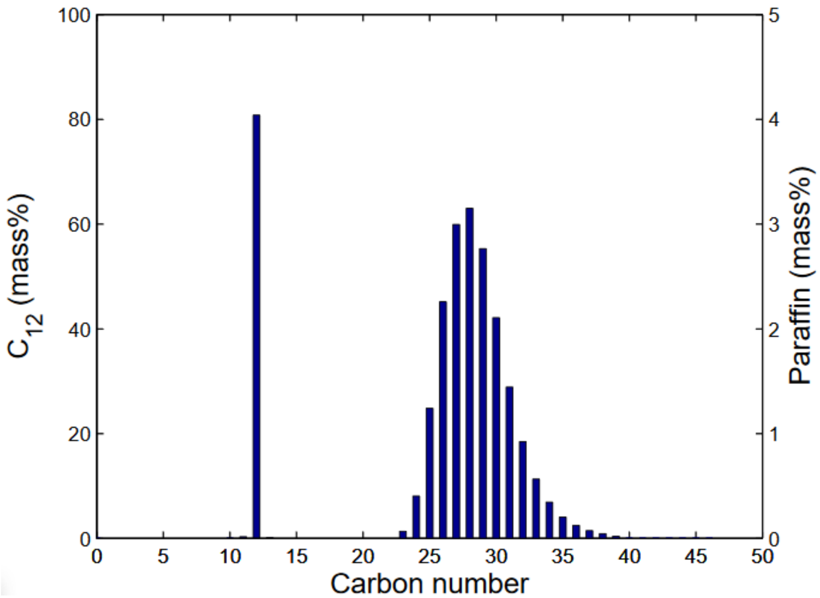

Figure 2. Mass based chromatography of the test fluid. Figure from Veiga et al. (2020)

Prior to the initiation of the experiment, water from the hot bath was pumped through the copper tube and the hot test solution was pumped through the annular region. The experiment began when, through a valve maneuver, cold water was directed to the copper tube, leading to the cooling of the surface in contact with the flowing paraffin, and the formation of a wax deposit around the copper pipe.

The flow rate was adjusted in the pump controller according to the desired Reynold number, which, in the present work, were 736, 1440 and 2073. After the formation of the wax deposit, a sample was removed from the inside of the test section and a high temperature chromatographic analysis (HTGC) was performed. The deposition experiments were performed for three different time intervals: 1 h, 3 h and 7 h.

Figure 3 illustrates the outer acrylic tube of the annular test section containing a port that allows sampling of the deposit. The port cover was removed after unscrewing four quick-release nuts, allowing access to the inside of the annular test section where de deposit had been formed. The probe to the right of the port was used the obtain temperature profiles. These results are not reported in the present paper.

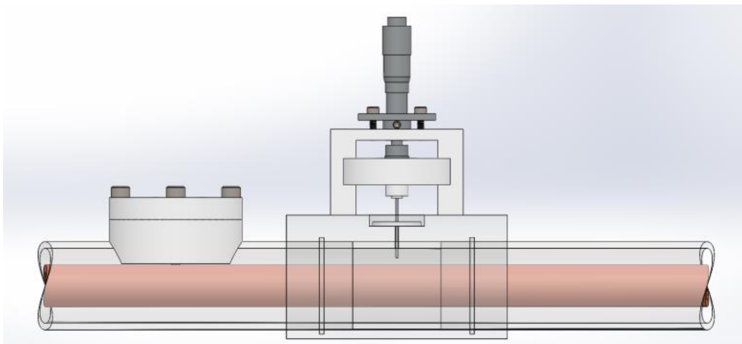

Figure 3. Port for sampling in the annular test section (to the left side). Figure from Veiga et al. (2020)

At the end of the experiment (1 h, 3 h or 7 h), the water from the tank where the test section was immersed was drained until it reached a level just below the sampling port cap. To minimize variation in the composition of the deposit after the flow was stopped for the port cap removal, the pump responsible for maintaining the solution flow was kept on, draining the solution from the annular region, and exposing the deposited wax. With the port open, access to the deposit was easy, as can be seen in the picture shown in Figure 4.

Figure 4. Open port showing formed wax deposit

A special device was constructed to sample the wax deposit trough the sampling port. Figure 5 shows images of the device fabricated from an acrylic cylinder, resembling the body of a syringe. At one of its ends the sampling device was machined with a curvature that matched the outside diameter of the copper tube. A special L-shaped metallic spatula was used to help in removing the deposit. The removed deposit can also be seen in Figure 5, inside the sampling device.

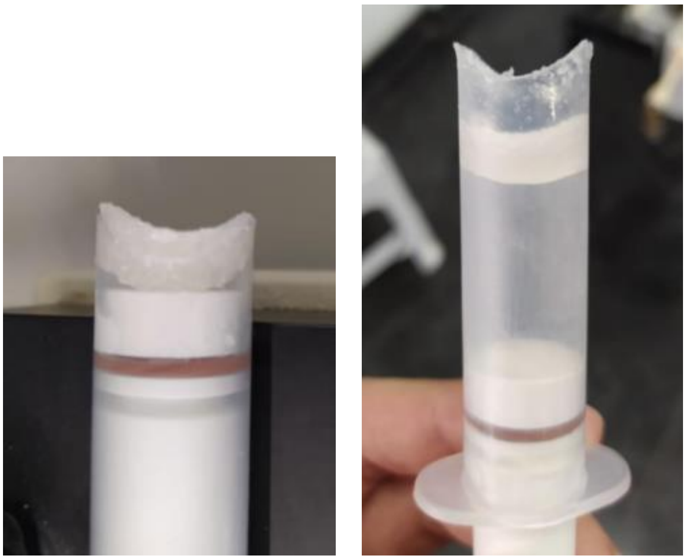

Figure 5. Wax deposit collected

The sampled wax deposits were then transferred to an air-tight sampling container and sent for chromatograph analysis. Two types of sampling experiments were conducted. Firstly, the samples of the deposits were analyzed as a whole, in order to verify the average aging of the entire deposit. In the second set of experiments the sampled deposits were sliced in half radially. The outer and inner halves of the sample were transferred to separated containers and sent to analysis. These experiments were conducted to study the radial variation of the deposit composition.

After sampling operation was completed, the port was closed, and the pump was restarted to fill the annular section with test fluid for the next programed experiment.

3. RESULTS AND DISCUSSION

In this section, the results obtained for the deposit composition will be presented as a function of the duration of the experiments, cold wall temperature and the flow rate.

The WAT for the test solution was 35.6°C, and the investigated cold wall temperatures were set at WAT-12.6°C and WAT-23.6°C. The duration of the experiments was 1 h, 3 h and 7 h, and deposits were sampled at these times. For each duration, three values of the Reynolds number were tested, namely, 736, 1440 or 2073.

3.1. Effect of experiment duration on the wax deposits composition

After 1 h, 3 h and 7 h, the experiment was stopped, and the deposits were collected, as already described. Figure 6 shows the concentrations of wax components in the samples obtained by using high temperature gas chromatography for various experiment durations. A comparison with the concentration of the initial solution is presented for reference purposes. The deposit samples did not include only the precipitated fraction, but also the solvent, C_{12}, that was entrained in the deposits. For the results presented in Figure 6 tests were performed for durations of 1 h, 3 h and 7 h with Reynolds number of 736 and a cold wall temperature of WAT-23.6°C, while Figure 7 shows the results for the Reynolds number of 1440 a cold wall temperature of WAT-23.6°C. The deposit aging phenomenon was also verified and confirmed by increasing the wall temperature to WAT-12.6°C, as illustrated by Figure 8.

An observation of the results of Figure 6 to 8 shows that the mass concentration of C_{12} decreases with the duration of the deposition experiments for different Reynolds number, as well as that of the light n-alkanes ranging from C_{22} to C_{24}. In this latter case, however, the decrease is more subtle. A much-pronounced increase is observed in the concentration of high molecular weight components, C_{26} to C_{39}. This is an indication that higher molecular weight components diffuse into the deposit while the lighter components diffuse out of the deposit. This behavior is well documented in the literature and characterizes the role of molecular diffusion in the deposit aging process.

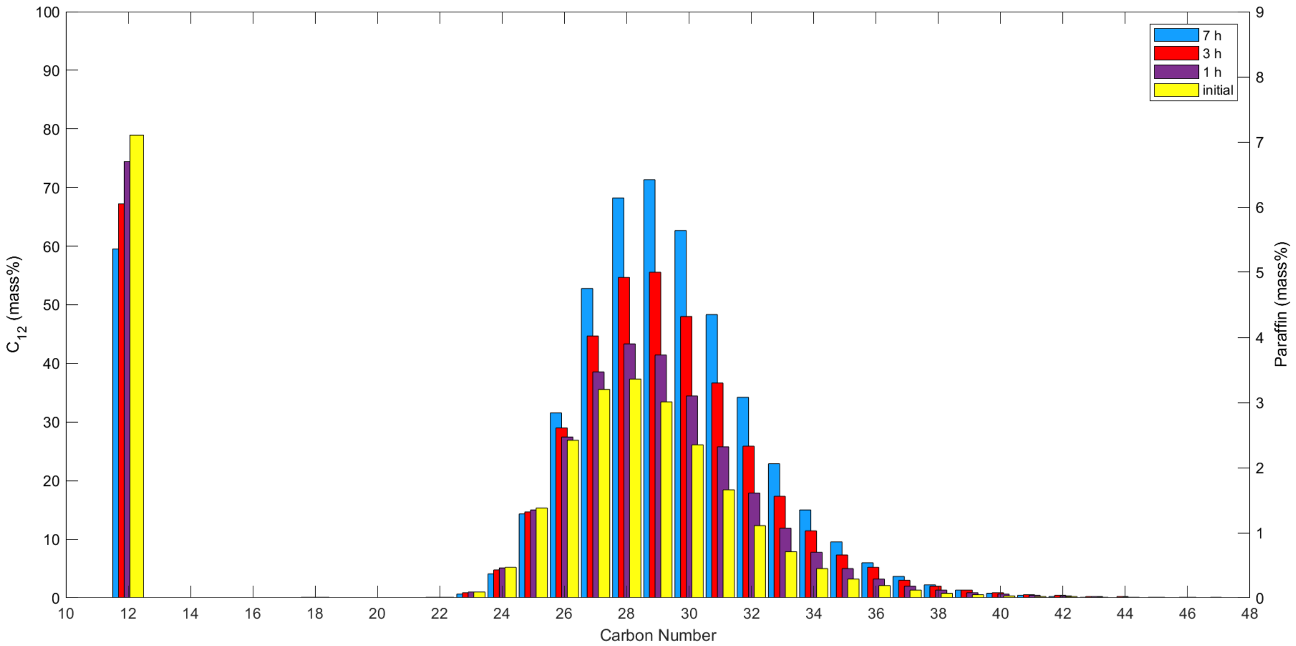

Figure 6. Mass fractions of wax components at various experiment durations, for WAT-23.6 °C and Reynolds number 736

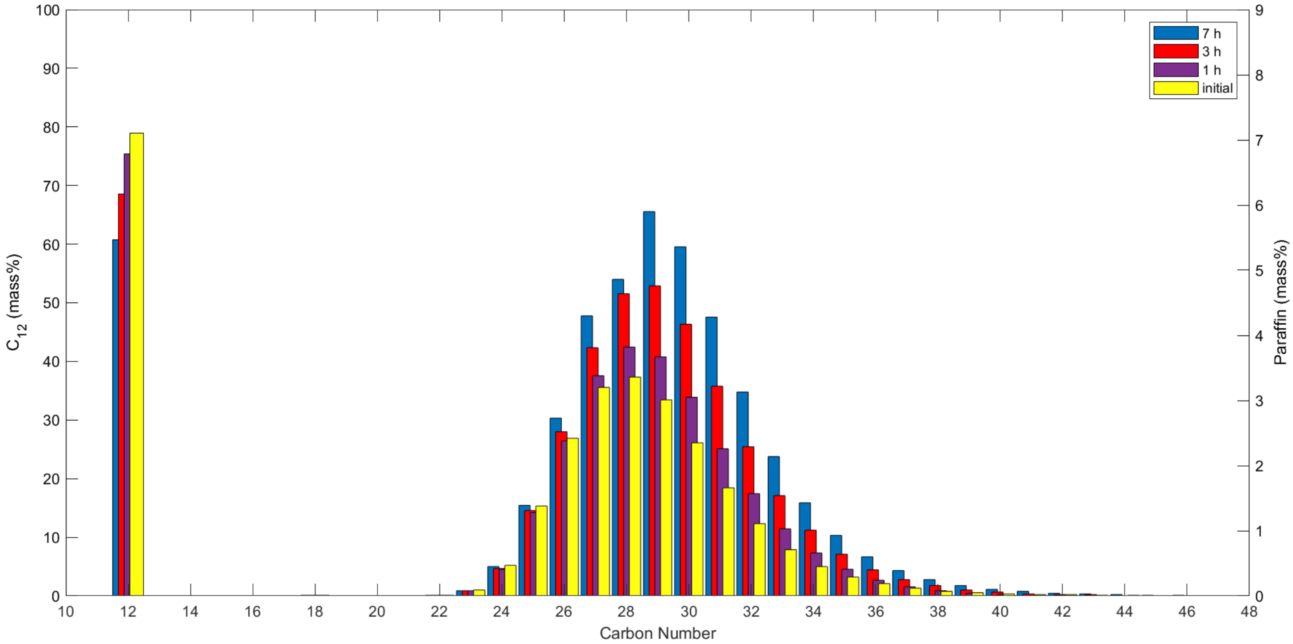

Figure 7. Mass fractions of wax components at various experiment durations, for WAT-23.6 °C and Reynolds number 1440

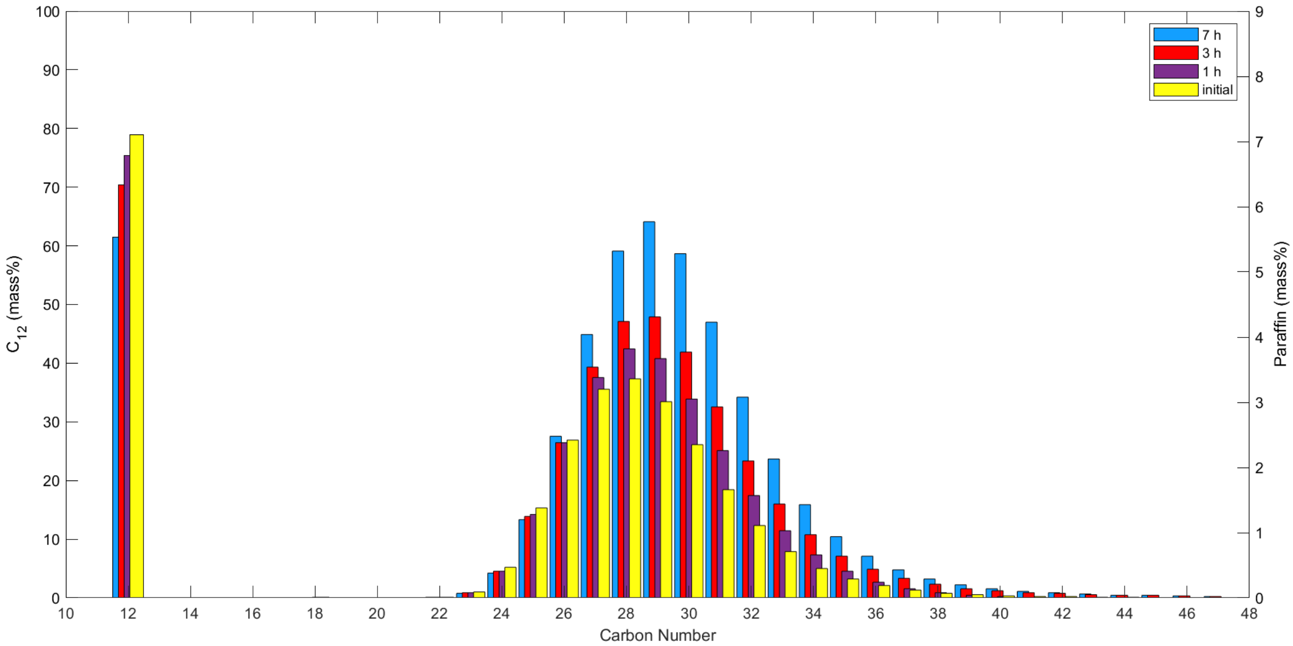

Figure 8. Mass fractions of wax components at various experiment durations, for WAT-12.6 °C and Reynolds number 736

3.2. Effects of wall temperature on the wax deposits composition

Figures 9 to 13 present the results obtained for deposit composition for two different wall temperatures, WAT-23.6 °C and WAT-12.6 °C. The results are presented for durations of 1 h and 3 h for Reynolds numbers of 736 and 1440. For Reynolds numbers of 2073 the data are for 1 h durations.

The results indicate that the variation of the cold wall temperature did not affect the composition of the deposits for experiments of 1 hour (Figures 9, 11 and 13). This is a somewhat surprising result, since it was expected that larger values of temperature difference imposed along the deposit would induce higher diffuse flows that, consequently, would produce variations in the composition of the deposit, as verified in the results of 3 h tests durations illustrated in Figures 10 and 12, for Reynolds number of 736 and 1440, respectively.

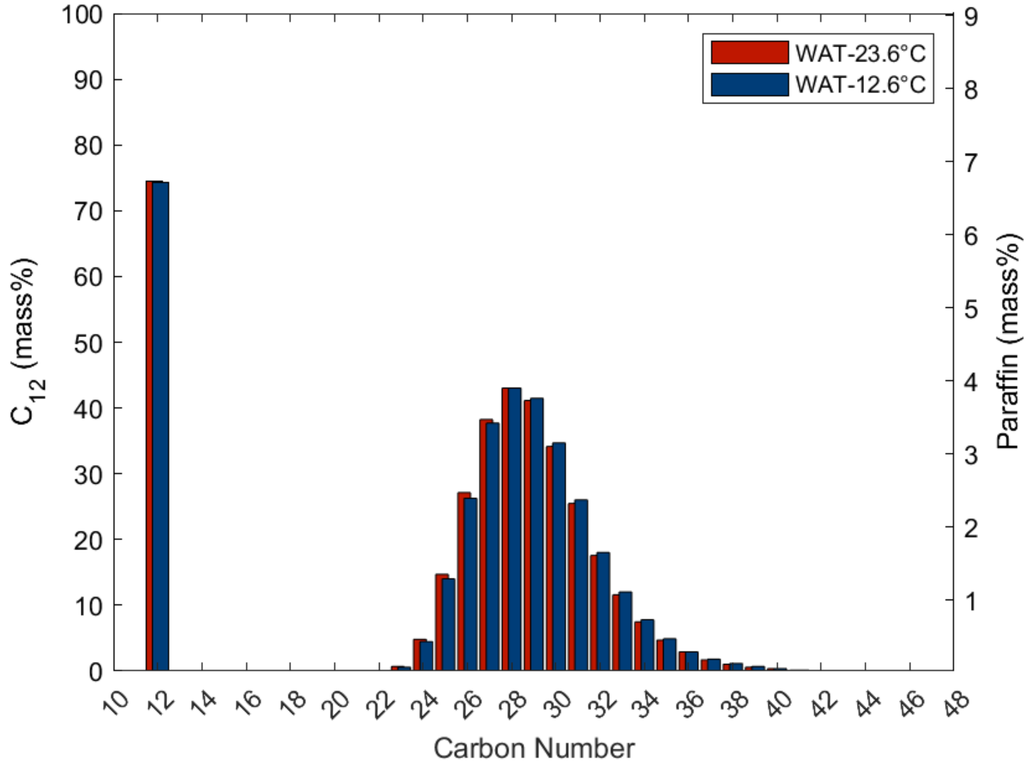

Figure 9. Mass fractions of wax components at different wall temperatures for Reynolds number 736 and 1 h of duration of the experiment

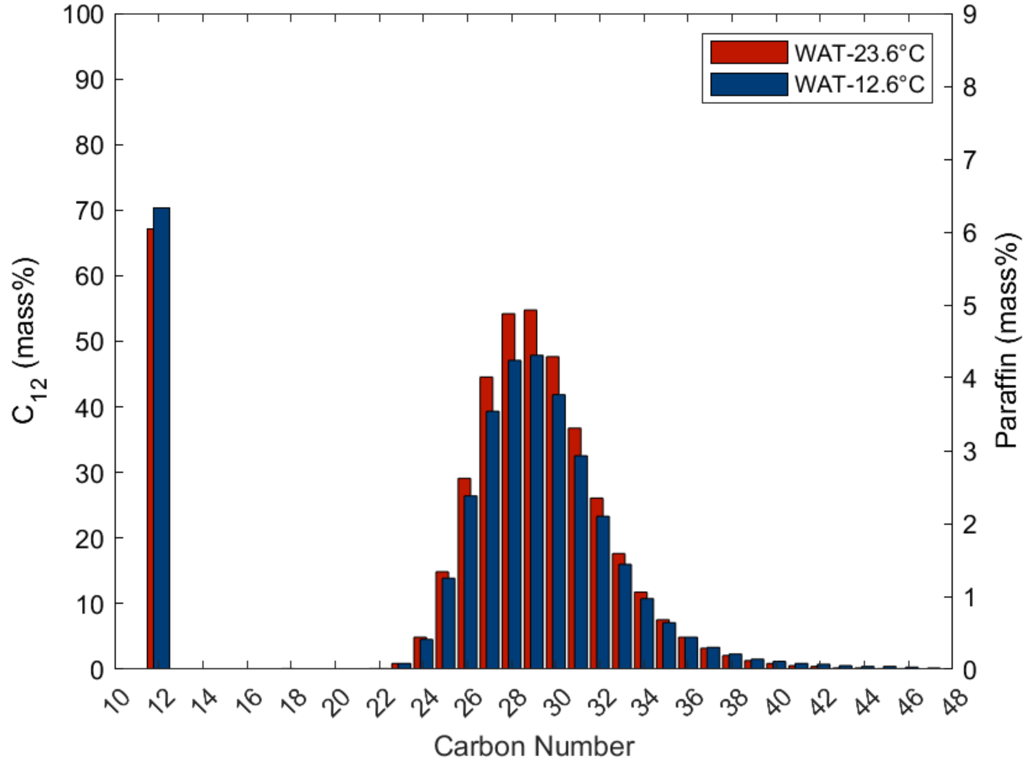

Figure 10. Mass fractions of wax components at different wall temperatures for Reynolds number 736 and 3 h of duration of the experiment

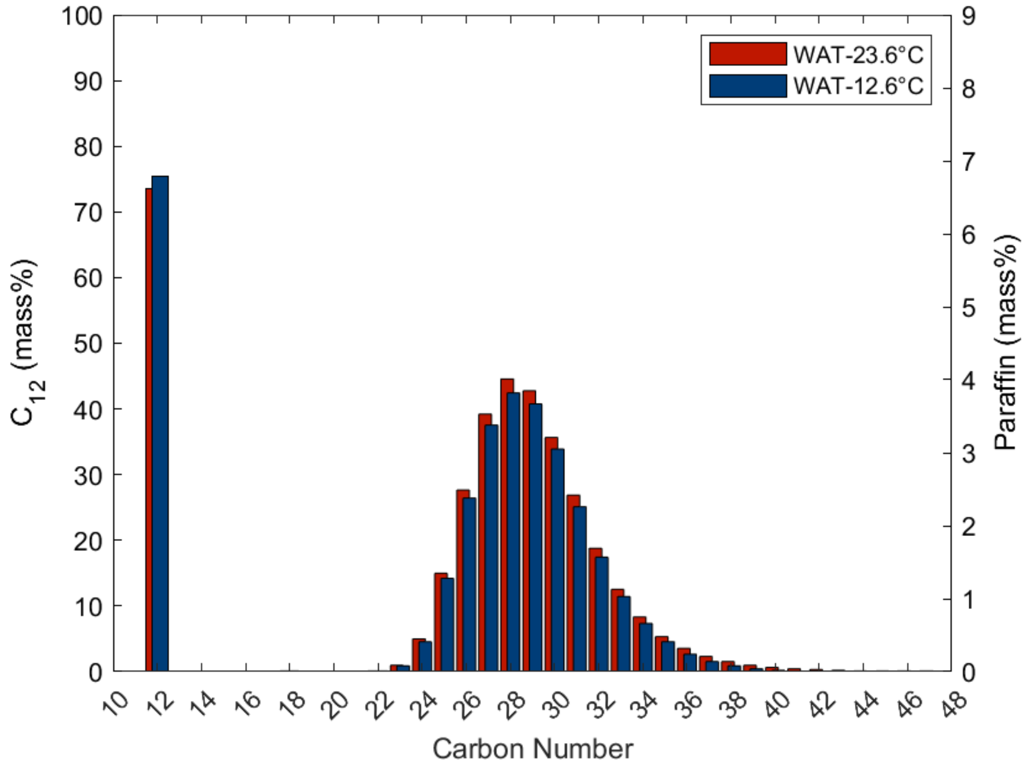

Figure 11. Mass fractions of wax components at different wall temperatures for Reynolds number 1440 and 1 h of duration of the experiment

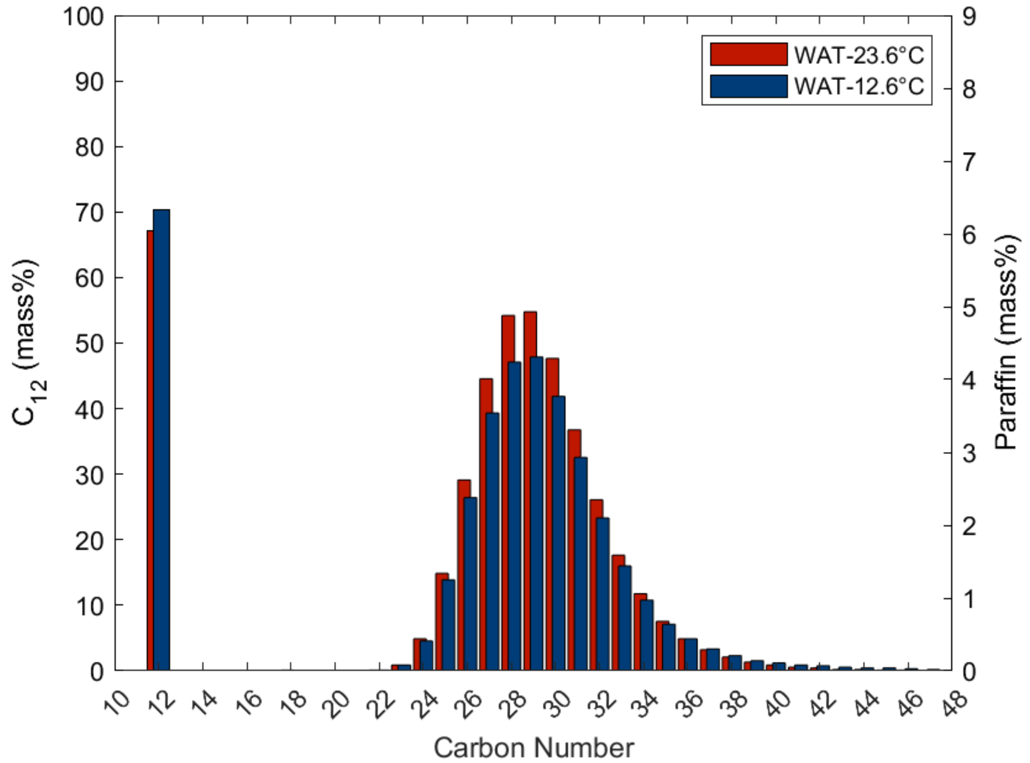

Figure 12. Mass fractions of wax components at different wall temperatures for Reynolds number 1440 and 3 h of duration of the experiment

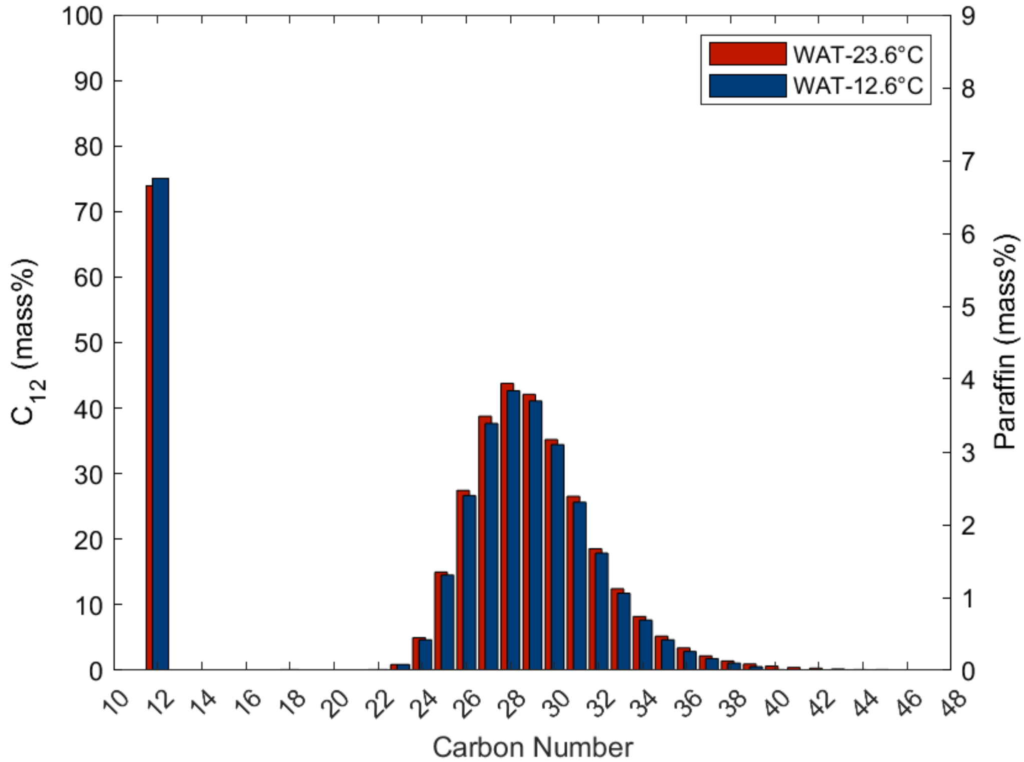

Figure 13. Mass fractions of wax components at different wall temperatures for Reynolds number 2073 and 1 h of duration of the experiment

3.3. Assessment of sliced deposits

For the study of the radial variation of the composition of the wax deposits, samples were sliced into an outer half, closer to the flowing oil and an inner half, closer to the cooled surface. The first case analyzed was for Reynolds number of 736 and 1 hour of deposition time. Figures 14 and 15 show a comparison between the two halves of the deposit, where it is possible to observe that the outer half has a higher concentration of heavier carbon fractions, indicating that the phenomenon of aging deposits may be more relevant for the deposit part that is exposed to the flow of hot paraffinic oil. To a lesser extent, Figures 16 and 17 reiterate this behavior for the Reynolds numbers of 1440 and 2073, respectively, for the 1-hour case.

One possible explanation for this lower aging of the deposition in the regions closer to the cold wall could be the fact that as a high cooling rate was used, the region immediately in the vicinity of the wall was exposed to this high cooling rate, resulting in a deposit with smaller, and thereby more packed crystals. Once the deposit starts to grow, the effective cooling rate above the deposit is reduced, resulting in the formation of larger and less packed wax crystals, which favors molecular diffusion. This rationalization needs further investigation.

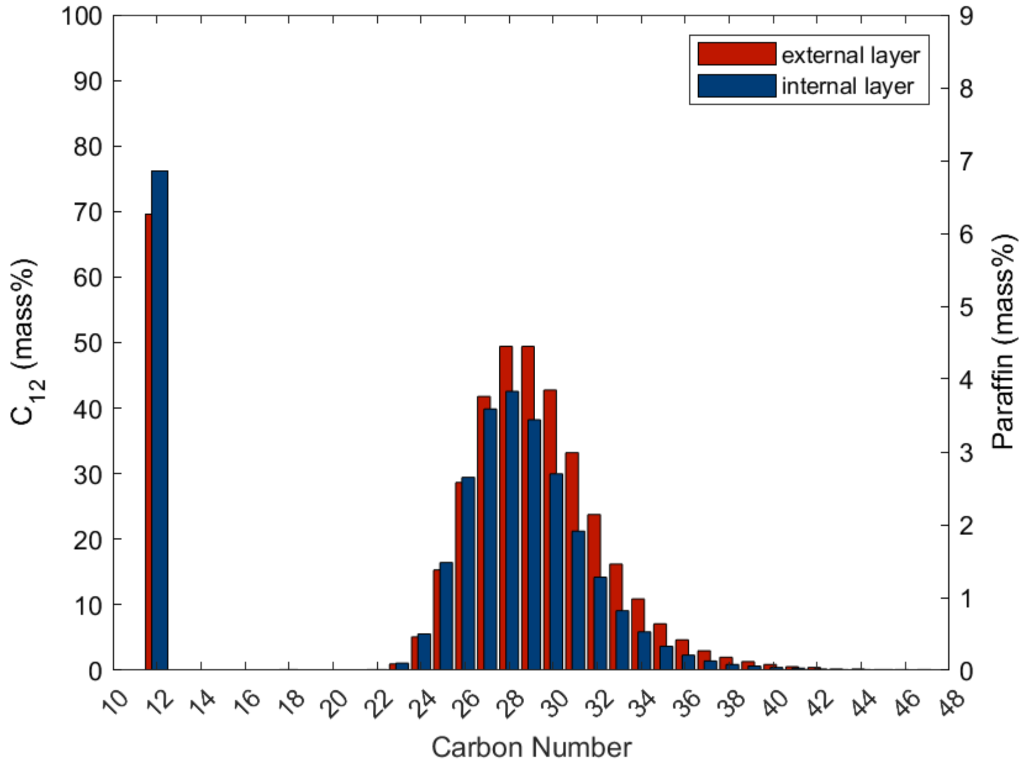

Figure 14. Mass fractions of wax components from the sliced deposit from 1 h of experiment, wall temperature at WAT– 23.6 °C and Reynolds number of 736

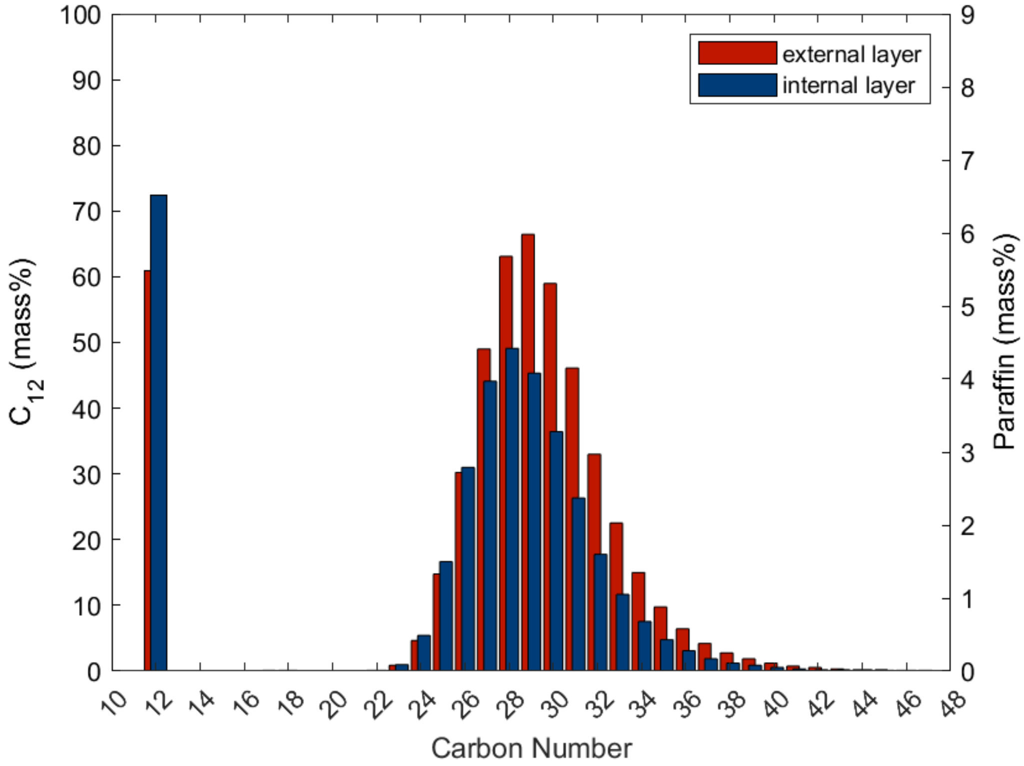

Figure 15. Mass fractions of wax components from the sliced deposit from 3 h of experiment, wall temperature at WAT-23.6 °C and Reynolds number of 736

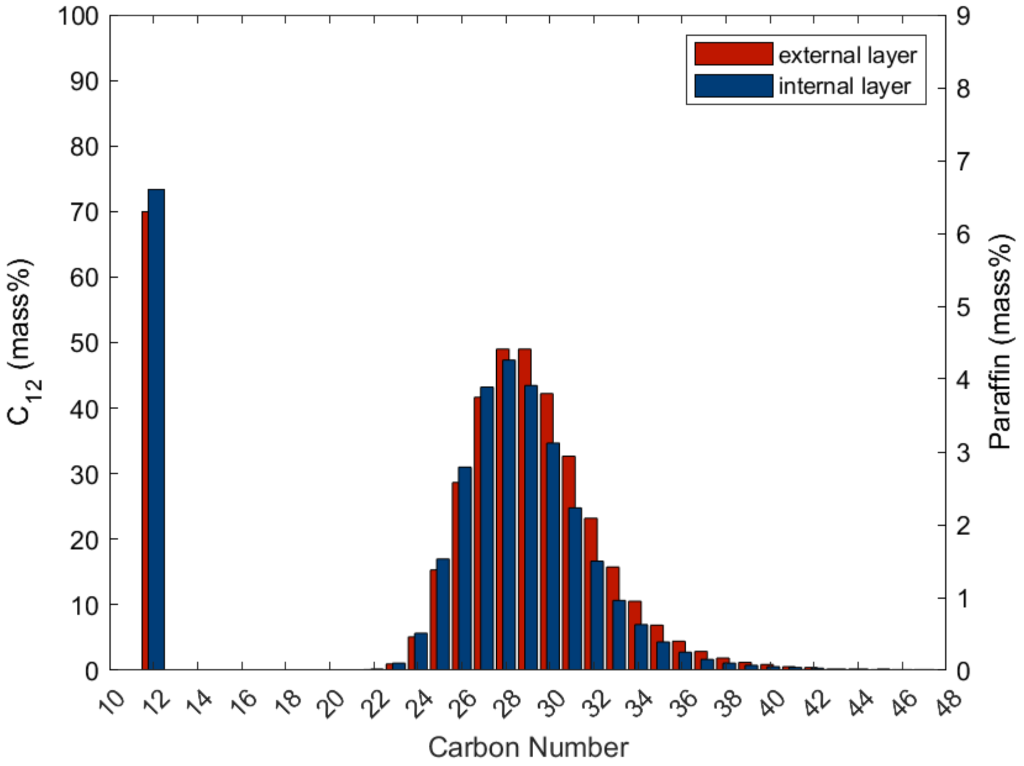

Figure 16.Mass fractions of wax components from the sliced deposit from 1 h of experiment, wall temperature at WAT– 23.6 °C and Reynolds number of 1440

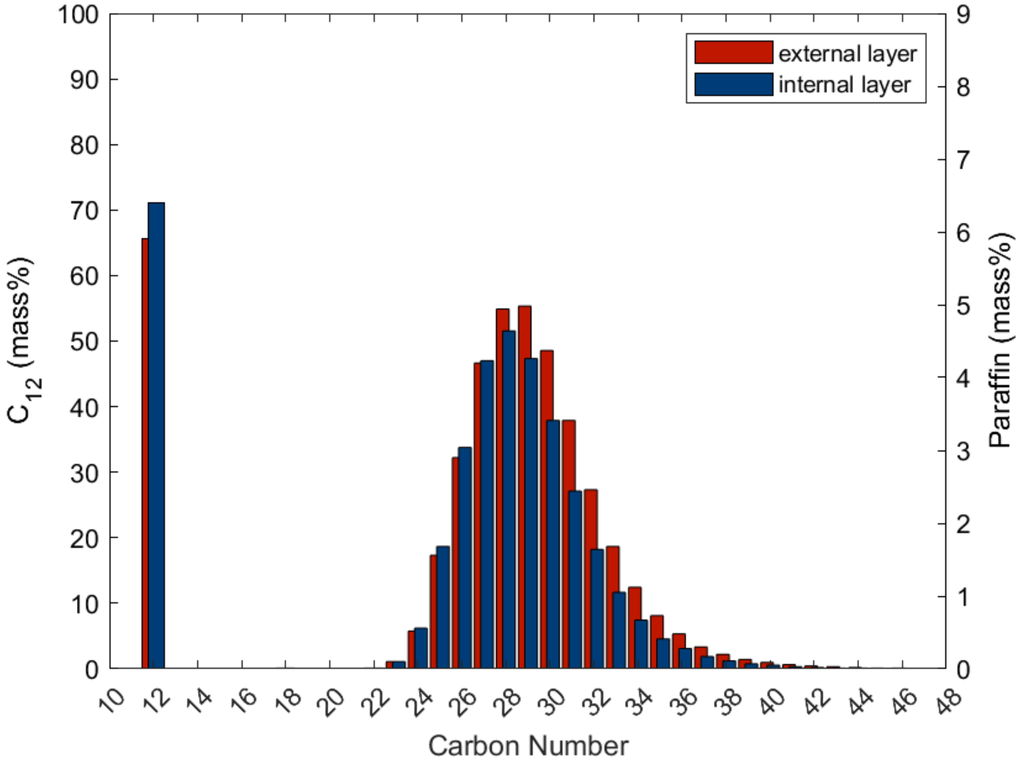

Figure 17. Mass fractions of wax components from the sliced deposit from 1 h of experiment, wall temperature at WAT– 23.6 °C and Reynolds number of 2073

Figure 18 shows a comparison between the inner part of the deposit for experiments of 1 h and 3 h, while Figure 19 makes a similar comparison for the upper part of the deposit slice. It can be observed that the time variation of the external part is much more accentuated. This fact indicates that the heaviest fractions tend to concentrate at the deposit-fluid interface because of the difficulty in penetrating the deposit due to the lower diffusivity of the components.

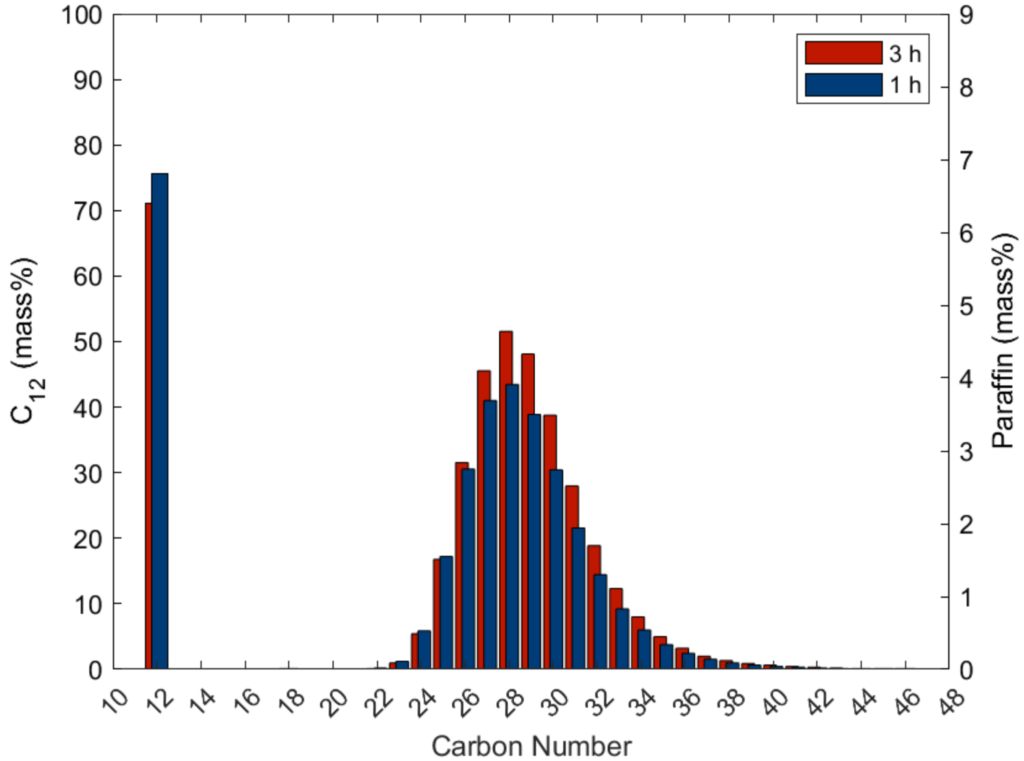

Figure 18. Comparison of mass fractions of wax components from the inner half deposit for 1 and 3 h of experiment duration, wall temperature at WAT-23.6 °C and Reynolds number 736

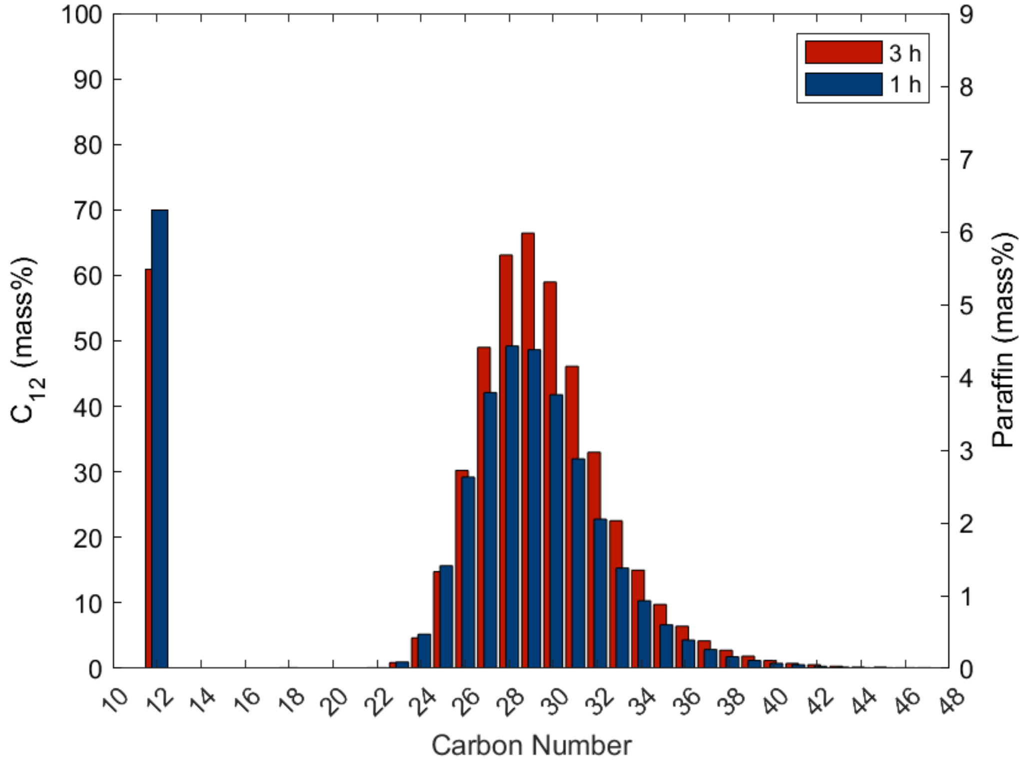

Figure 19. Comparison of mass fractions of wax components from the outer half deposit from 1 and 3 h of experiment, wall temperature at WAT-23.6 °C and Reynolds number 736

4. CONCLUSIONS

The present work investigated the temporal and radial composition variation of wax deposits samples formed at 1 h, 3 h and 7 h of duration of the deposition experiments. The tests also included experiments at different wall temperatures set at WAT-23.6°C and WAT-12.6°C. Assessing the effect of different flow rates represented by the Reynolds numbers of 736, 1440 and 2073 is still inconclusive and requires further analysis. The enrichment of the heavy fractions characterizing the phenomenon of aging of the deposit was confirmed for the longer experiments. There were no significant differences in the mass contents of the different wax components in the deposits when varying the flow rate and the cold wall temperature.

Radial variations of the deposit composition were assessed by slicing the deposits into two radial pieces, the outer piece closer to the flowing warm solution and the inner piece closer to the cold wall. The results indicated that deposit aging occurred mainly in the outer half, while variations were more subtle in the inner half.

5. ACKNOWLEDGEMENTS

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