

Sample Preparation for Unconventional Analysis: A Case Against Solvent Extraction

Jon Burger, Doug McCarty, Russ Peacher, and Timothy Fischer
Chevron Energy Technology Company

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ABSTRACT

Porosity differences have been shown previously between the two general techniques used for processing unconventional samples, retort extraction and solvent extraction for saturation. The differences are typically 1-2 porosity units (PU) but can be higher. This is significant in 4-8 PU systems. In the unconventional analysis world, there are two schools of thought for porosity measurement, one is measuring the bulk volume and gas filled pore space, then adding the water and oil volumes removed by retort extraction, thermal extraction to 700°C (1300°F). The second is to measure the bulk volume and then a conventional grain volume after solvent extraction (Dean-Stark extraction with toluene followed by methanol soxhlet extraction). The pore volume is then calculated using the difference in the bulk and grain volumes. Standard practice for solvent extraction is approximately 7 days of toluene extraction at approximately 110°C (231°F) to fully remove the water and clean the sample.

Some have suggested the aforementioned porosity difference is attributed to the removal of structural water (hydroxyl groups) from the clays by the long term solvent extraction. This seems unlikely because clay hydroxyl groups are only removed at temperatures well above 200°C (392°F). X-Ray Diffraction (XRD) analysis shows no evidence (*e.g.* shift in peak position) for the occurrence of this phenomenon. The difference in the porosity values from the two techniques is likely due to dissolution of organic matter by solvents during Dean-Stark extraction. The portion of the organic matter removed is immobile, not thermally extractable below 200°C (392°F), but is solvent extractable. Results of porosity measurements from a variety of test types and preparation conditions are reviewed. In addition, supporting analytical measurements such as XRD, TOC/Rock Eval, Thermogravimetric Analysis (TGA), Subcritical Nitrogen surface area and pore size analysis and Mercury Intrusion Capillary Pressure (MICP) are included.

INTRODUCTION

The standard workflow for core processing is typically, gamma log, optional CT scanning for orientation and core quality, slabbing followed by drilling plugs for routine analysis. The plugs are then cleaned, oven dried, and, finally, measured. Conventional techniques typically use Dean-Stark extraction for water volume measurement followed by methanol

and/or chloroform-methanol azeotrope in a Soxhlet extractor to do the final cleaning and leach the salt. All the methods are well described in the API RP-40 document on Recommended Practises for Core Analysis. Several of the labs use the same approach for unconventional plays. The goal is obtaining water saturation followed by total porosity.

In unconventional plays, two variations have emerged for obtaining water volumes for saturation and pore and bulk volumes for porosity. The conventional approach is used by several labs. The bulk volume and bulk density is measured using an Archimedes approach. This is followed by 5-7 days in a Dean-Stark apparatus with boiling toluene at 110°C (231°F) to clean and obtain water volume. This is followed by methanol extraction and oven drying. The grain volume is measured, the total porosity calculated using the grain and bulk volumes, the saturation calculated from the Dean-Stark water volume, oil volume from mass change difference in Dean-Stark, and the remainder is the gas volume.

A second approach measures the bulk volume similarly, the gas filled volume of crushed material in the current state by helium expansion followed by retort at three temperatures, 120°C, 315°C, and 700°C (250°F, 600°F, and 1300°F). The retort collects the water and oil volumes. These are all well documented in the API RP 40 and the Luffel GRI report. Gas filled pore volume plus oil volume plus water volume gives total pore volume and thus porosity. Error issues arise when oil or water volumes are under reported at the middle temperature.

This work evaluates the errors associated with solvent extraction techniques. A series of evaluation steps were conducted in parallel to assess the impact. A series of 1-foot core sections were slabbed vertically to make four equivalent quarter sections. Each quarter section was sent to a different vendor and one kept within Chevron. The vendors were instructed to measure bulk density, grain density, porosity, permeability, and fluid saturation.

Additionally, a series of tests were conducted using a Thermogravimetric Analyzer on natural, Dean-Stark Extracted, and Thermally extracted samples. RockEval/TOC and Subcritical Nitrogen pore size analyses were also conducted for each sample.

RESULTS AND DISCUSSION

Data from the round robin study is presented in Figures 1-4. Porosity values measured by two vendors using the Dean-Stark method (Vendors 1 and 2, Figure 1) are comparable. Vendor 3, using a retort method, measured porosity values up to 2 PUs lower than the Dean-Stark method. Vendor 1 is shown as the X-axis data. One proposed explanation for this deviation in porosity measurements between the two methods is that the Dean-Stark method dehydroxylates clay minerals in the sample. If this is true, the total water volume evolved from the sample measured by the Dean-Stark method would necessarily be higher than from retort. This is not the case. In fact, the total water volumes are nearly identical between the three vendors (Figure 3).

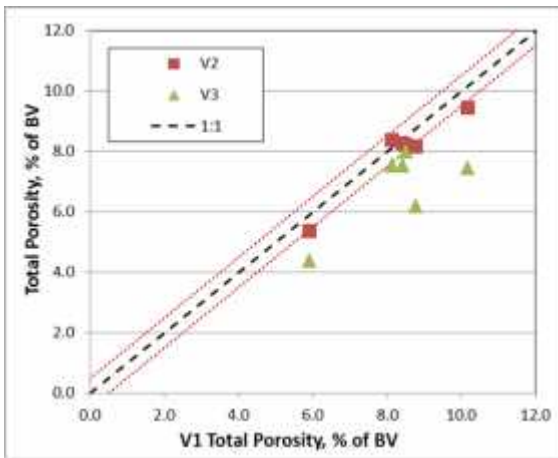


Figure 1: Comparison of measured porosity from three vendors.

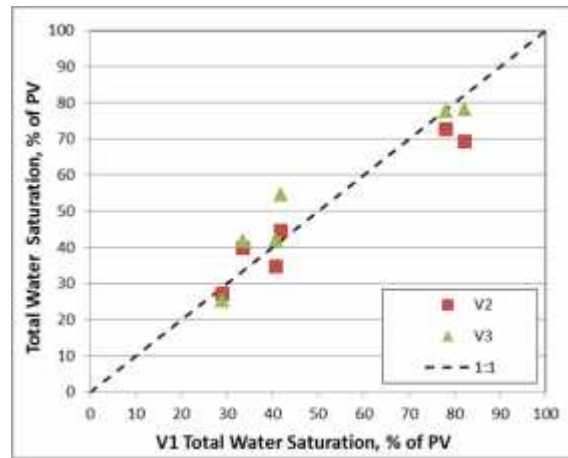


Figure 2: Comparison of measured water saturation from three vendors.

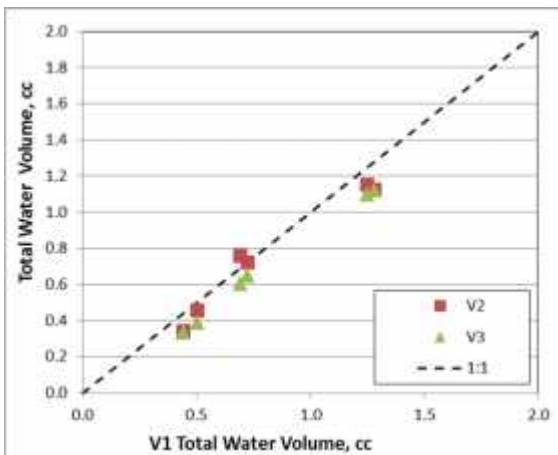


Figure 3: Comparison of measured water volume from three vendors.

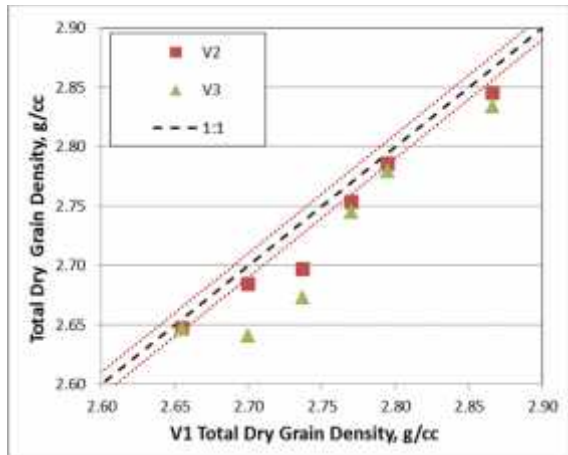


Figure 4: Comparison of measured dry grain density from three vendors.

X-ray diffraction analysis provides more conclusive proof that the Dean-Stark method is not dehydroxylating the clay minerals. Drits *et al.* (2012) demonstrated what structural transformations occur in a 2:1 layer clay mineral upon dehydroxylation (Figure 5). In a sample measured by XRD prior to and after Dean-Stark extraction no change that could be attributed to dehydroxylation is evident (Figure 6). Indeed, the XRD patterns are essentially identical.

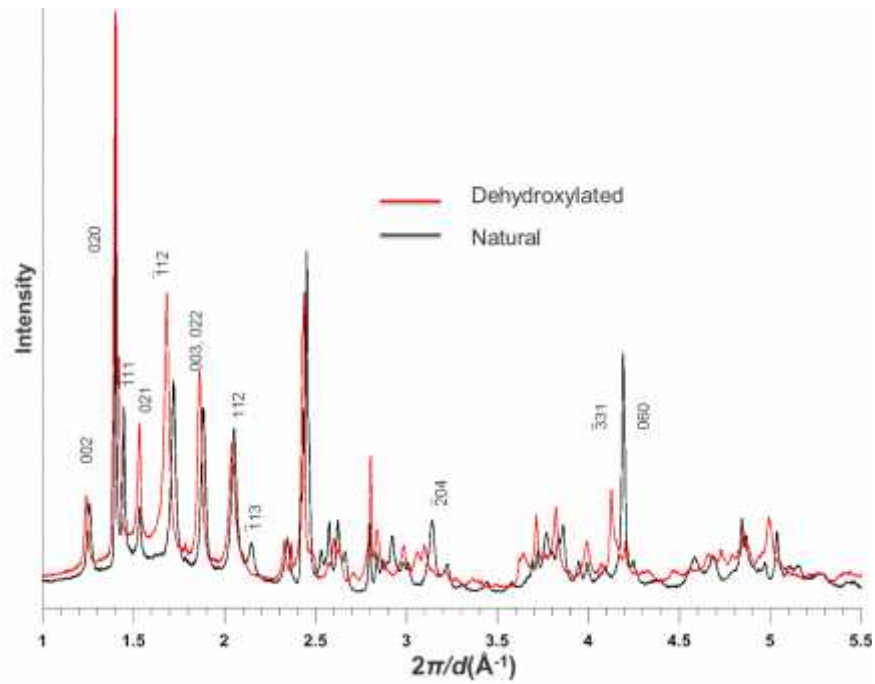


Figure 5: XRD pattern showing shift in clay peaks due to dehydroxylation. Drits, McCarty, & Derkowski (2012) American Mineralogist, 97, 1922-1938.

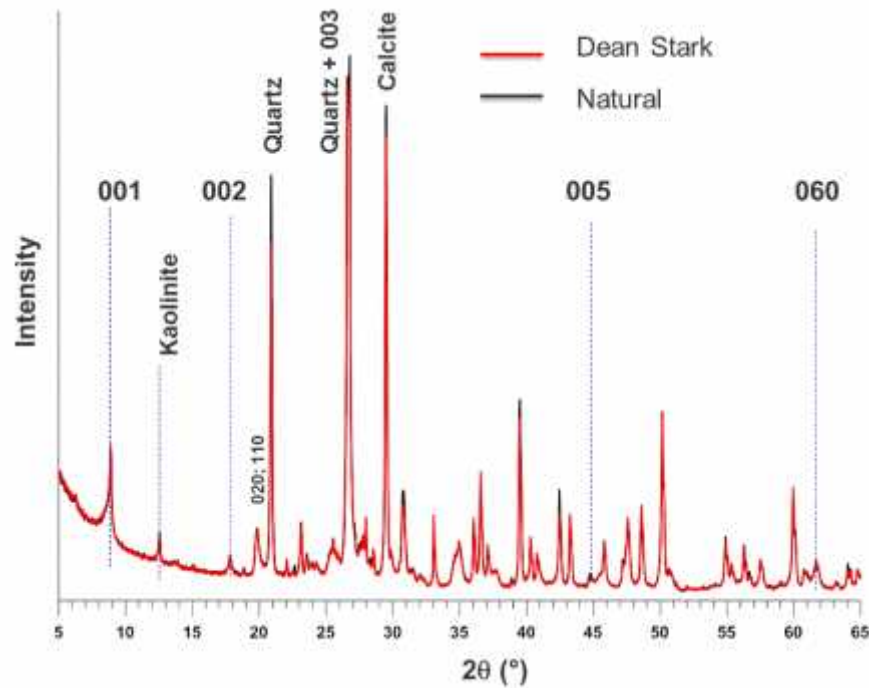


Figure 6: XRD pattern showing no shift in clay peaks before and after Dean-Stark Extraction.

The dehydroxylation of clays during Dean-Stark is not, then, an explanation for the difference in porosity seen in Figure 1. An alternate explanation is that the Dean-Stark method creates porosity by removing soluble organic matter (SOM). Figure 2 shows that the water saturation measured by Dean-Stark is never larger than the water saturation measured by retort and can be significantly smaller. With similar total evolved water volumes, that can only occur if the pore volume is increased in the Dean-Stark samples.

A porosity comparison between the Dean-Stark method and Water Immersion Porosity (WIP) was conducted by Kuila *et al.* (2014, Figure 7). The grain densities measured by both methods are equivalent in samples with low TOC. In the high TOC samples (>4%) a significant deviation is observed – measured grain densities are up to 0.15 g/cc higher as measured by Dean-Stark. Organic matter has much lower density than mineral grains and this would increase the grain density of the sample upon removal. The larger grain density would equate to a larger porosity and would explain the data in Figure 1.

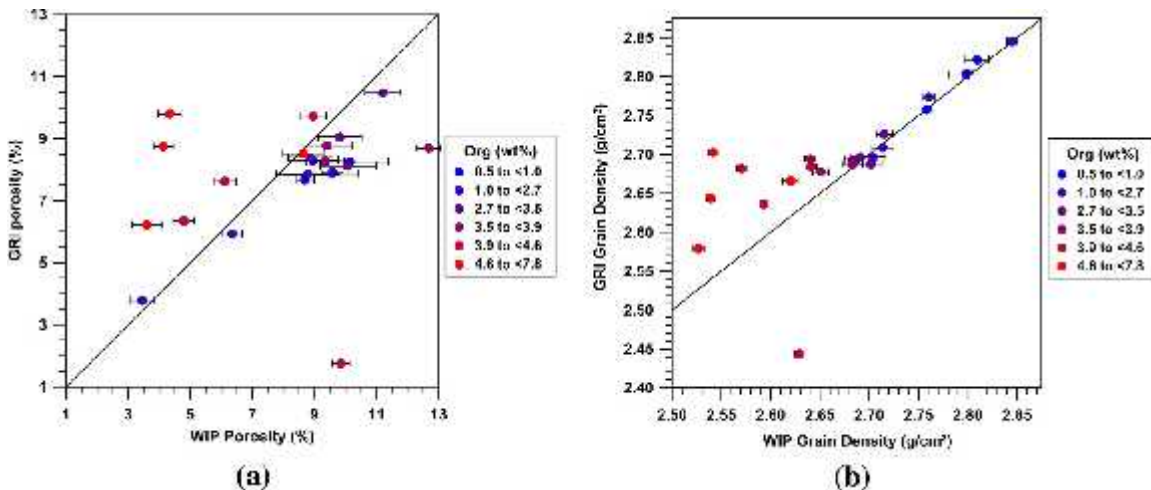


Figure 7: Comparison of (a) measured total porosity and (b) measured grain density of the samples from SS2 by the WIP and GRI techniques. The 1:1 comparison line is marked by dotted line in the plots. Kuila *et al.* (2014)

RockEval, Thermogravimetric analysis (TGA), and Subcritical Nitrogen Gas Adsorption (SGA-N₂) analyses were performed to test the hypothesis that Dean-Stark extraction was removing soluble OM. The solvent extraction removed most of the S1 and half of the S2 in the organic matter (Table 1, Figure 8). The TOC value was reduced by 15%. The Dean-Stark treatment removed the entire S2 hydrocarbon in the low-temperature region (4-8 min).

Table 1: RockEval/TOC data from a natural and Dean-Stark extracted sample.

| | S1 | S2 | S3 | TMAX | LECO TOC | HI | OI |
|------------|------|------|------|------|----------|-----|----|
| Natural | 3.74 | 3.59 | 0.27 | 459 | 2.71 | 132 | 10 |
| Dean Stark | 0.63 | 1.74 | 0.32 | 451 | 2.38 | 73 | 13 |

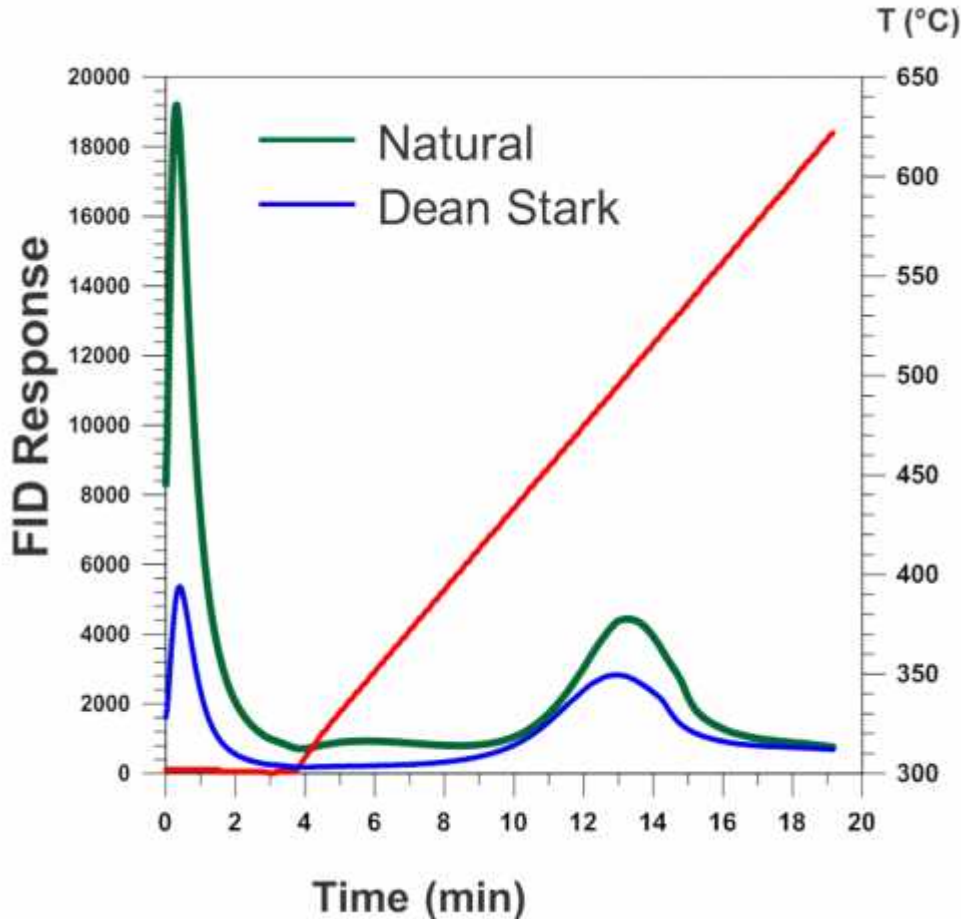


Figure 8. Impact of Dean-Stark extraction on the RockEval/TOC results. It shows the Dean-Stark removes most of the S1 and S2 components for this sample. Preparation by Thermal Extraction removed the S1 but not all of the S2.

The extraction of moveable hydrocarbons is important to properly measure the porosity of a sample. A Thermal Extraction technique (TE; heating to 200°C) was developed to enable removal of free water, clay bound water, and moveable hydrocarbons but retain the clay structural water and solid-phase hydrocarbons. TGA of Dean-Stark and TE have different behavior in regards to the removal of hydrocarbon from a sample (Figures 9-10). Both methods remove most of the components of OM below 400°C (752°F), while Dean-Stark treatment removes a significant portion from the

400-600°C (752-1112°F) temperature range. TE removes a much smaller amount in that temperature range. OM in the high temperature range is thought to behave more like rock matrix than recoverable hydrocarbon – it occupies porosity but is not considered part of the original hydrocarbon in place or reserves.

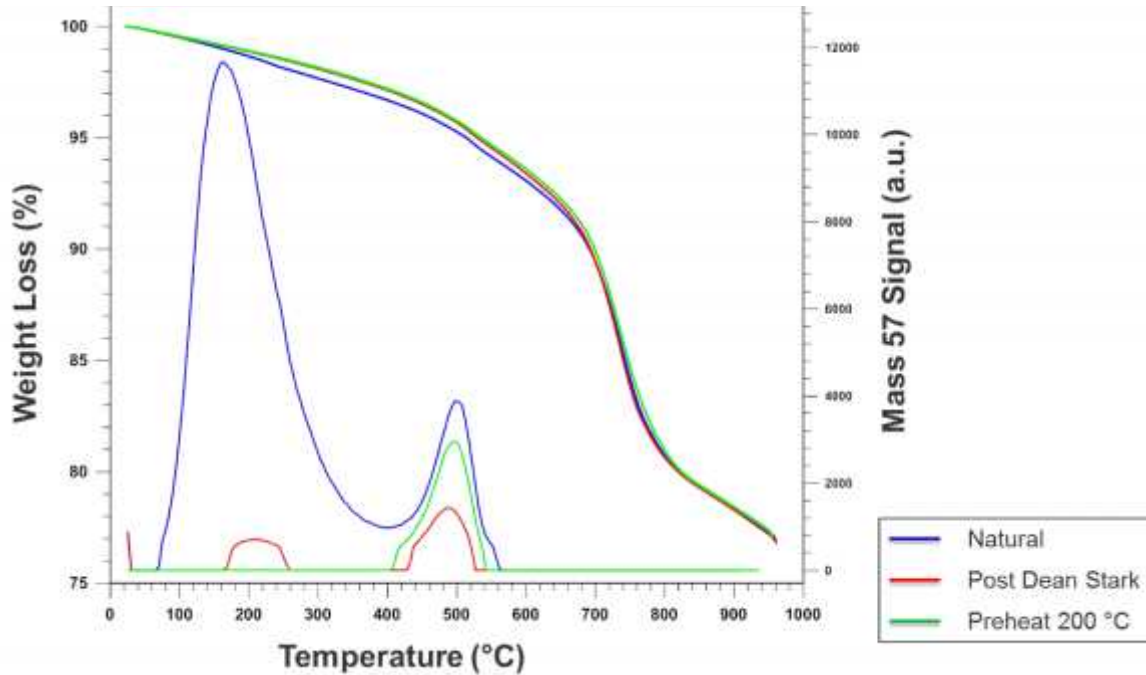


Figure 9: TGA patterns showing differences in peak heights and widths based in the natural, thermally extracted, and Dean-Stark Extracted samples.

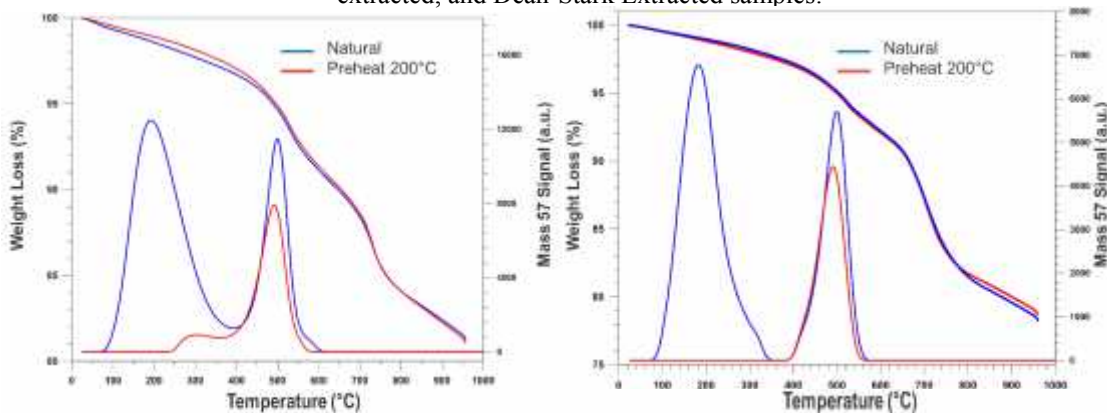


Figure 10: TGA patterns showing differences in peak heights and widths based in the natural and thermally extracted samples showing consistent preservation of the 400-600°C organic matter.

The last piece of evidence that supports the hypothesis that Dean-Stark treatment removes OM and artificially increases porosity is a direct measurement of the pore-size distribution by SGA-N₂. The Dean-Stark extracted sample had a larger number of pores across the entire pore-size range (Figure 11). The TE sample had a larger number of pores in the small pore range (<80 nanometers) but less than the Dean-Stark extracted

sample. The removal of organic matter by the Dean-Stark shows an opening of the entire pore system to greater porosity and permeability. The increase in permeability would have a compounding effect on the porosity measurement.

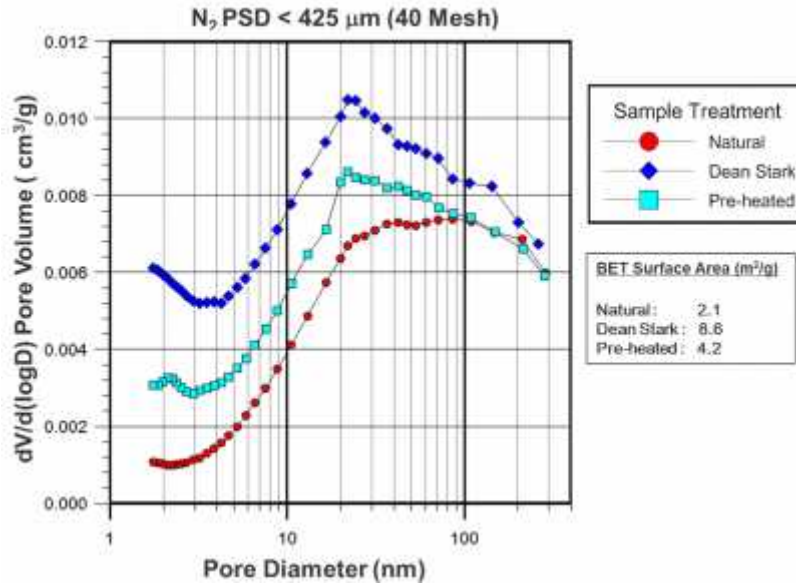


Figure 11: Pore size distribution comparison of natural, Thermally Extracted and Dean-Stark Extracted samples.

CONCLUSION

A round-robin porosity measurement experiment was conducted to determine the differences in two industry-wide methods, retort and Dean-Stark extraction. Dean-Stark extracted porosities were consistently higher than retort, by as much as 2 PU in a 4-8 PU system. The explanation that Dean-Stark creates porosity by clay mineral dehydroxylation was shown to be infeasible given the absence of any clay mineral structural transformations by X-Ray Diffraction analysis. Furthermore, the same amount of water is evolved from equivalent samples regardless of the method used.

The most likely reason for the higher measured porosity from Dean-Stark is that the extraction removes solid-phase Organic Matter and is actually creating porosity. This was demonstrated by grain density comparison with Water Immersion Porosity, direct measurement of evolved hydrocarbon by RockEval, direct measurement of solid samples by Thermogravimetric Analysis, and direct measurement of pores by Subcritical Nitrogen Gas Adsorption analyses.

The Dean-Stark extraction process, therefore, changes the properties of organic-rich material and has a large impact on the nature of the pore network. This creates a higher degree of uncertainty on the measurements and is likely overestimating porosity.

Property measurement by retort or a modified version of the retort method should be included in all core analysis programs. Sample preparation by Thermal Extraction for other analyses, MICP, SGA-N₂, WIP, etc., shows promise in that the organic matter is preserved to a higher degree.

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