PRODUCTION OF HYDROGEN CONTAINING FUEL COMPOSITES OVER POLYOXIDE AND HETEROPOLY ACID CATALYSTS

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The data on synthesis of hydrogen from propane-butane mixture and methane are presented. Optimum conditions for synthesis at a variation of reaction temperature, composition of catalyst, contents of active phase, ratio of reacting ingredients are determined.

KARACHAGANAK FIELD - INNOVATIONAL METHOD OF DIRECT DETERMINATION OF SATURATES-WAXES-AROMATICS- RESINS-ASPHALTENS BY TLC-FID TECHNIQUE

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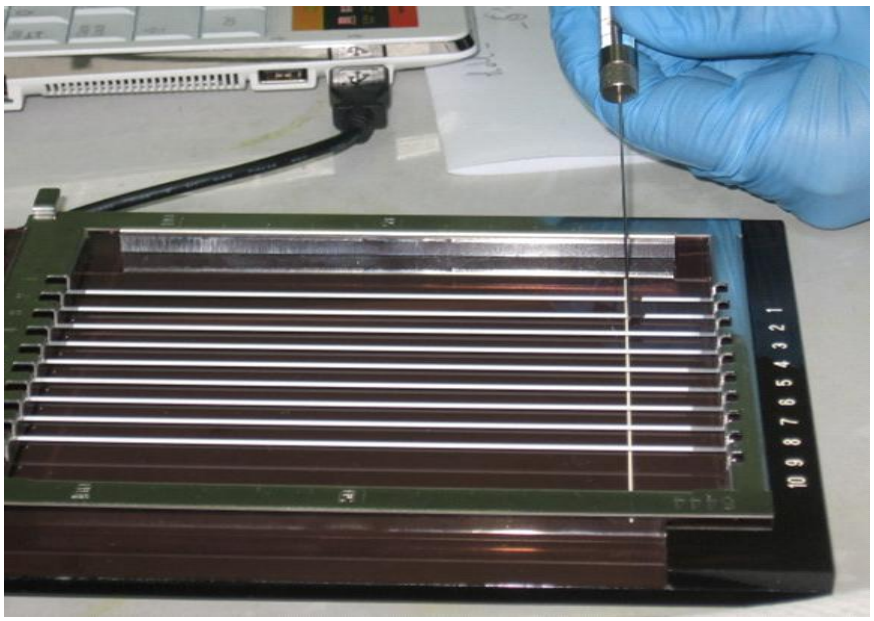
Based on separation of fluid compounds on the thin bonded layer of absorber (the stationary phase is a Chromarods – quartz rod with a silica surface) by means of the selective solvents (mobile phase) combined with technique of ionization of separated compounds by Flame Ionization Detector (FID), the KPO b.v. Chemical Laboratory could achieve direct separation of crude oil sample in one run into 5 compounds qualified as SWARA (Saturated-Waxes-Aromatics-Resins-Asphaltenes)

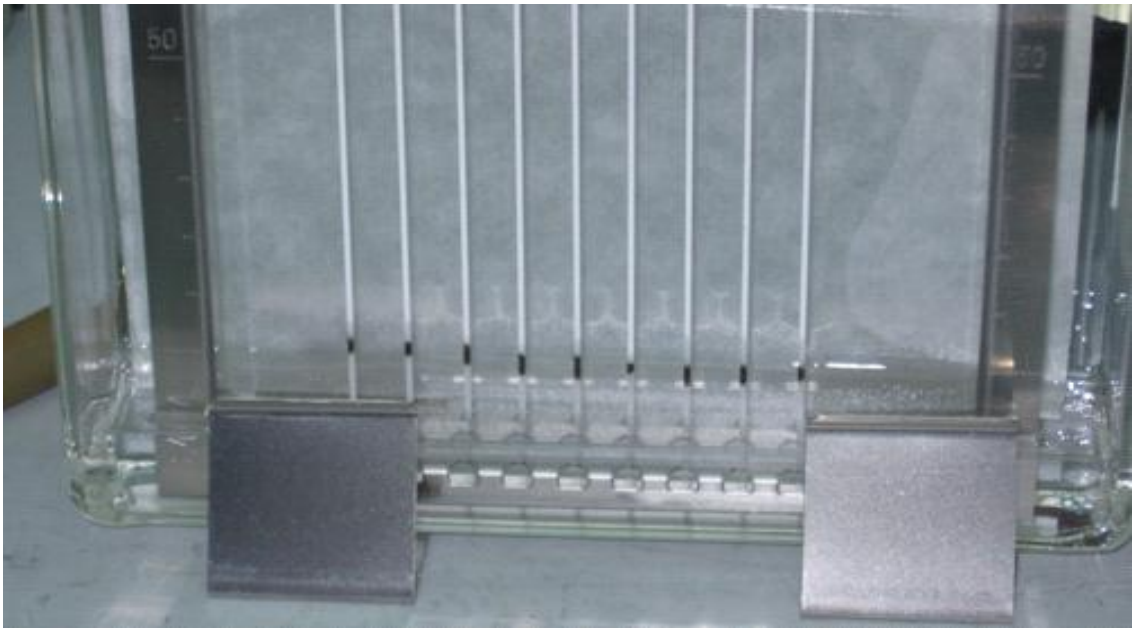
As a reference of performed research work was taken the "IP 469/D1 - standard method for determination of saturated, aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionization detector" performing the analyses on "Iatroscan MK-6" instrument. Conducted program can be subdivided in several steps summarized as following:

Preliminary steps – method verification: in order to get familiar with technology and instrument a different number of test runs, that has involved different type samples, variation of implemented solution's ratios, concentrations and elution sequences. During this to preliminary phase was possible to obtain three and four compound chromatogram according to IP 469/D1 and SARA (Saturates-Aromatics-Resins-Asphaltenes) method, specifications.

Secondary step – methodic optimization: In order to obtain good separation of compounds on chromatograms and define the right dilution ratio were chosen three different aliquots of KPO crude oil and diluted in solvent (0.05 g, 0.1 g, 0.15 g in 10 ml of dichloromethane). Different prepared aliquot were then spotted on chromarods (picture 1) and straight eluted (picture 2)with different agent, begun with heptane (70 ml), then a mixture of toluene/heptane (70 ml) in ratio of 80:20 volume percentages and finally a mixture of dichloromethane /methanol (70 ml) in ratio of 95:5 volume percentages. The chromarods (after terminate elution process) were passed on ionization process (FID burns chromarods providing signal proportional of eluted substances on chromarods) obtaining four peak and respective component determination, according to SARA method. In compliance with obtained results / chromatograms (example in Figure 1), the optimal concentration of aliquots was established approximately 10 mg/ml.



Picture 1 – Sample spotting



Picture 2 – Sample elution

During this phase were analyzed 29 samples of stable fluids sampled from 29 wells on “Iatroscan MK-6” as a proof test. Solution of each sample with approximately concentration 10-12 mg/ml diluted in dichloromethane were prepared and analyzed by SWARA method

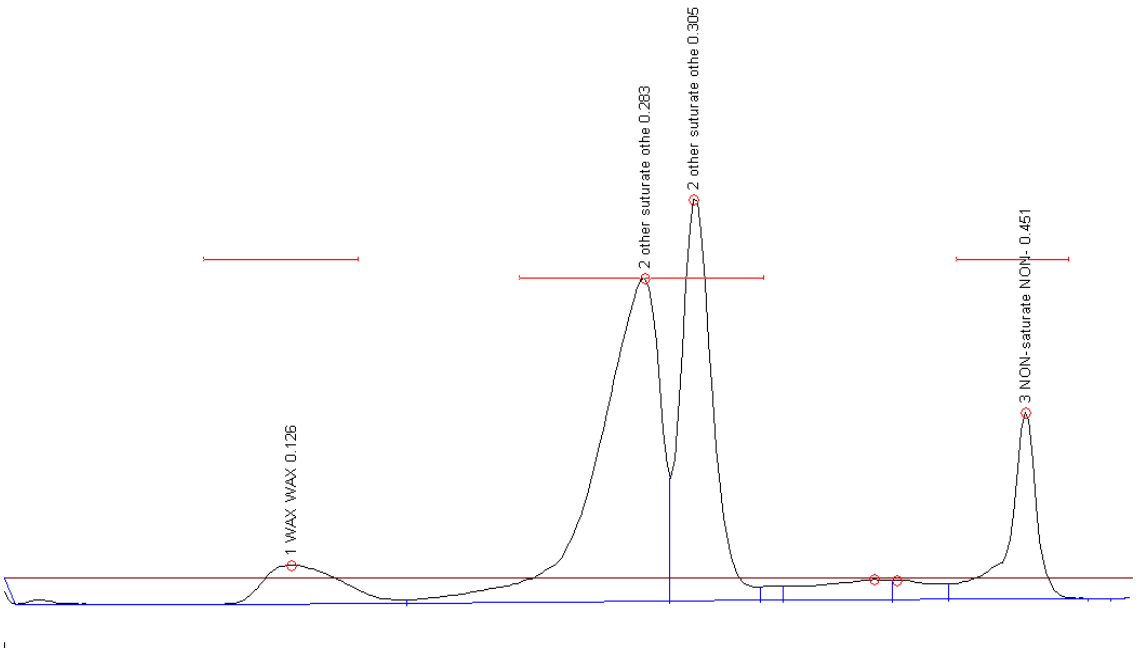


Figure 1 – Chromatogram of ionized oil sample by SARA method

Third step – SWARA separation**:** The primary scopes (last step) of research work was to obtaining speciation of sample in 5 components with one analyses (run) according to Xiaohu – Kalman – Redelius /2/ research job that initiate the SWARA (Saturates-Waxes-Aromatics-Resins-Asphaltenes) qualification. Basing our test on previous performed steps, a oil sample (0.1 g.) was dissolved in dichloromethane, then spotted onto chromarods (Picture 1), then it was eluted consequently in heptane (70 ml), in a mixture of heptane/toluene (70 ml ratio 20:80 volume percentages), and in a mixture of dichloromethane /methanol (70 ml ratio 195:5 volume percentages). At this point we had applied a back elution (in order to separate waxes form saturates) with acetone (80ml, cold). Eluted compounds were ionized by FID detector achieving the desired separation. (Figure 2)

Eluting (Picture 2) procedure was performed by straight and back elution.

Additional step – light fraction losses: Considering that standard method available are normally dedicated to heavy oil or asphalt testing, in our case one of the major aspect / question of this research work was to understand the crude oil behavior (KPO type), possible losses (quantitative difference in light fractions), that could occurs when sample spotted on chromarods (that contain light fractions) has been exposed to temperature (45 C per 15 minute) during the chromarods drying procedures. In order to verify the supposed changes, was tentatively simulated the evaporation process of different fractions of stable condensate from Chromarods during first step of Iatroscan analyses (drying). At this purpose a defined equal quantity of crude oil (previously analyzed by GC for obtained the composition content) was placed in different type of ceramic crucibles (by weight, diameter and design), then those were exposed at constant temperature and for defined amount of time (as per standardized procedure for SWARA testing). Remaining oil after the treatment were collected in vials and analyzed by gas chromatography technique. As a result was possible to observe the influence of heating on sample light fractions. Confirming that the trend of losing of light fractions is the same for all crucibles (but by different quantities), respectively.

Looking to the general results and graphical representation on figure 3, the mayor loss influences lighter fraction at least up to C6-C7 group, on figure 4 were developed a comparison that enhance light part differences.

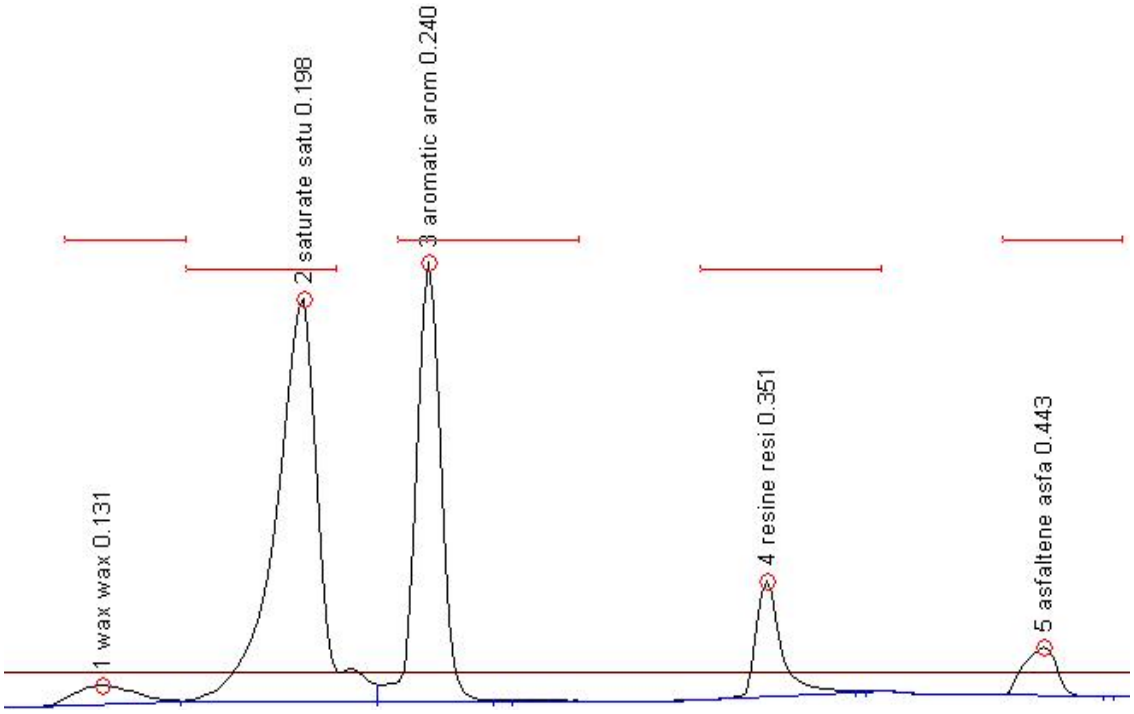


Figure 2 – Chromatogram of ionized oil sample by SWARA method

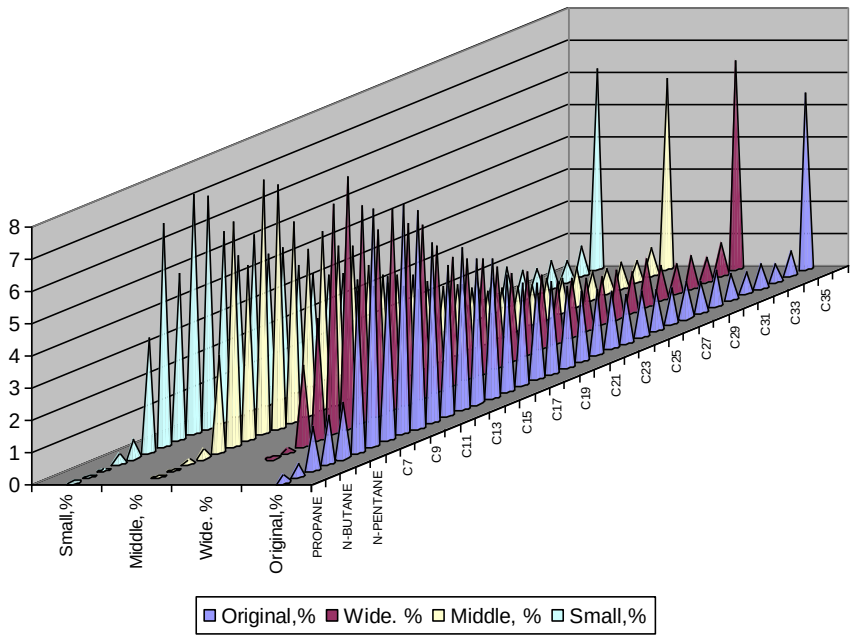


Figure 3

Difference of loss light fraction can well evidenced on below chromatogram obtained comparing the performed Gas Chromatograph analyses (most open crucible) in figure 5 and figure 6.

Final step – Calibration and future development: At this stage of research work due unavailability of dedicated calibration standards, KPO Chemical laboratories using a pure reference sample of wax (GSO for Waxes by GOST method) achieve qualitative and quantitative calibration of instrument. Actually in process research of other pure component or standard that will allow us to obtain an absolute calibration of all separated class of components.

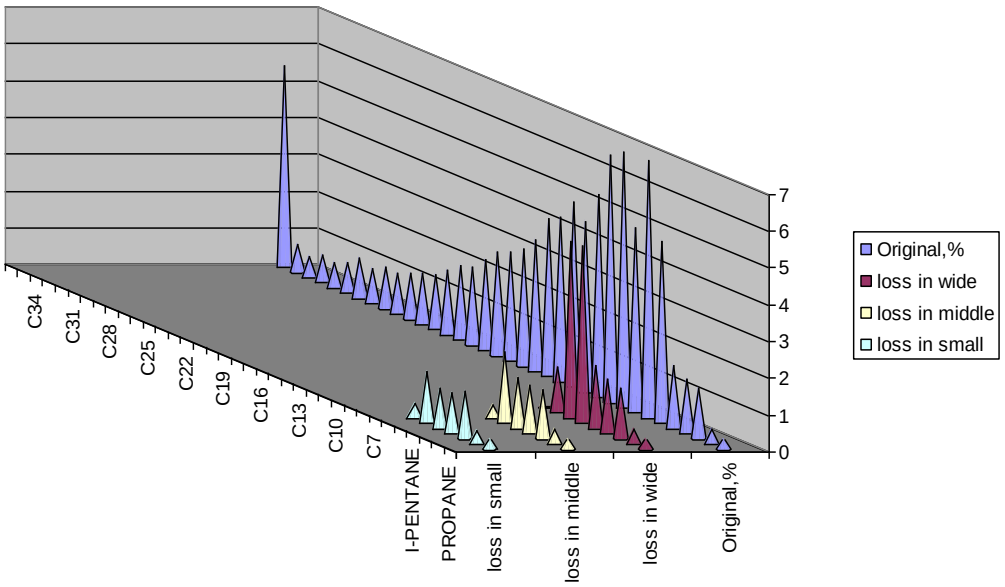


Figure 4

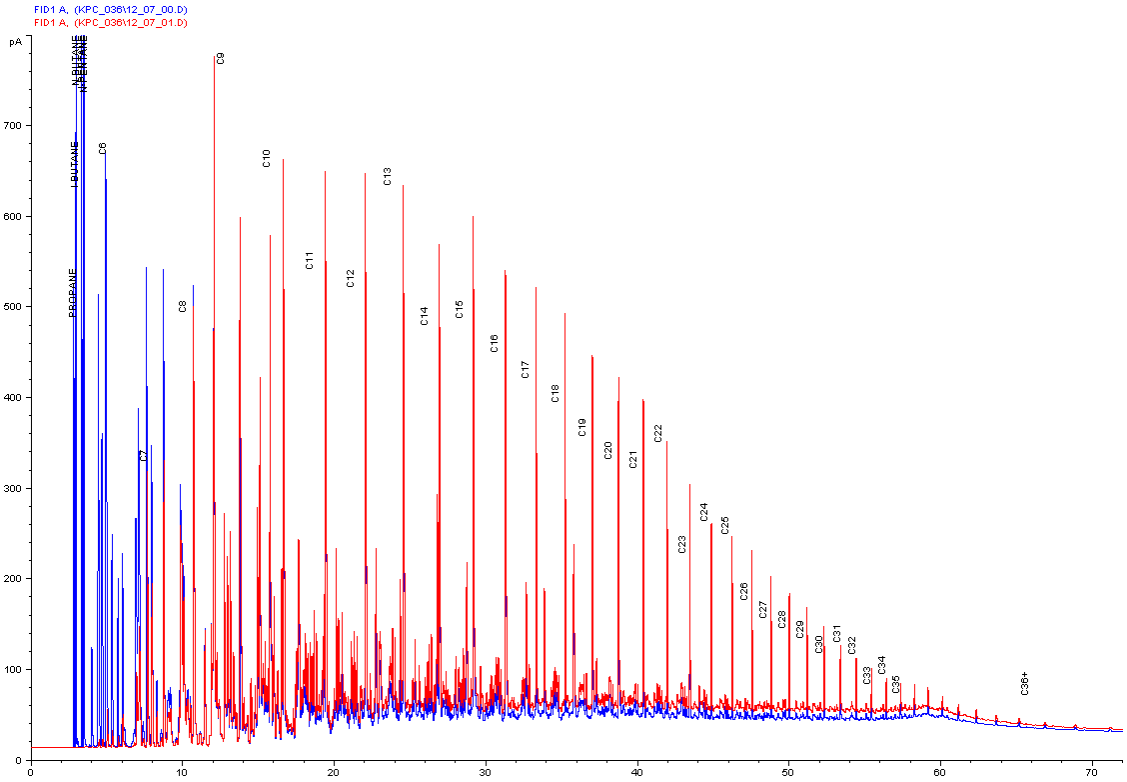


Figure 5

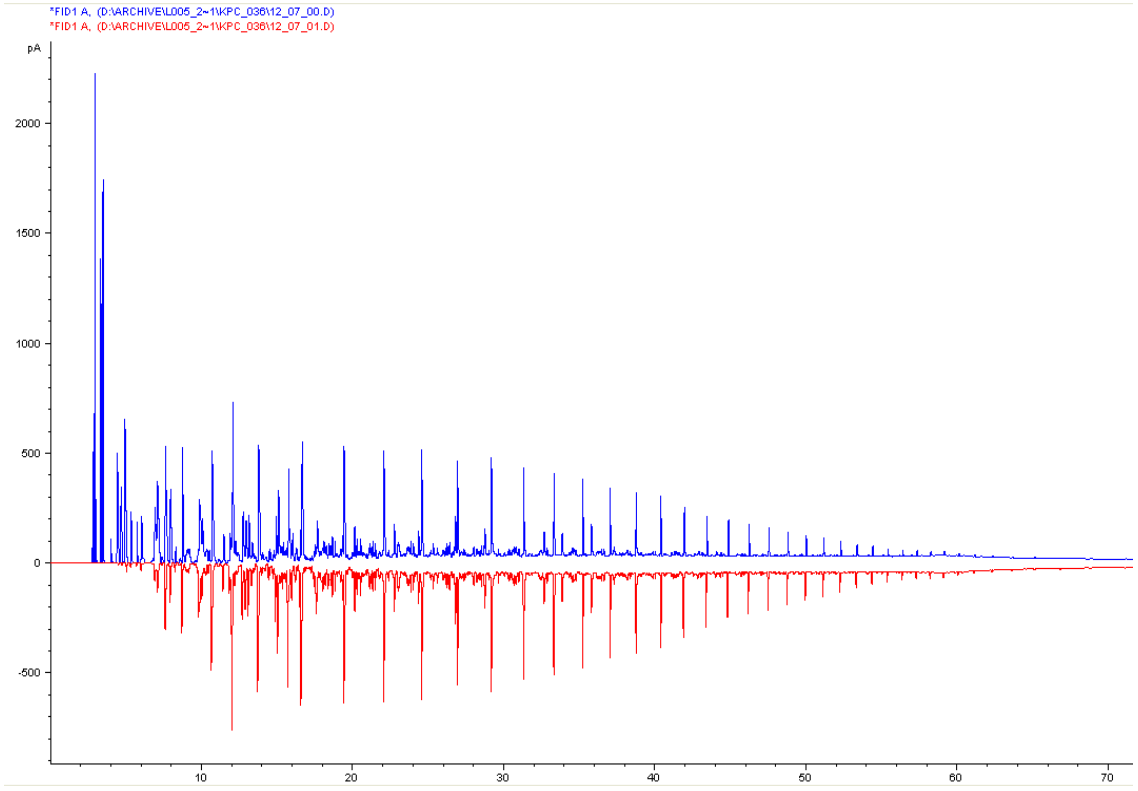


Figure 6

Concluding: TLC-FID technique combination showed a good repeatability and lower error, comparing wet chemistry process. Collected results prove us that in future using of Iatroscan MK-6, for determination of SWARA or single wax content in stable petroleum samples will be adaptability.

Advantages of the Iatroscan use defined during those tests:

- TLC-FID used for waxes determination (also including preparation phases), is faster then actual GOST in use (2 hours against 17);
- Consumes much less amount of solvents and sample;
- Any single sample is spotted on different chromarods (minimal 5 maximal 10) allowing parallel analyses;

In conclusion, those set of trials, confirm the possibility to utilize “Iatroscan MK-6” (with TLC-FID technique) with a dedicated method to perform analyses of Saturated-Waxes-Aromatics-Resins-Asphaltenes in one run and shortest time with a good analytical quality.

Reference

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ҚАНЫҚҚАН КӨМІРСУТЕКТЕР-ШАЙЫРЛАР –АРОМАТТЫҚ ҚОСЫЛЫСТАР-ПАРАФИНДАР-АСФАЛЬТЕНДАРДЫҢ ТҮЗУІН АНЫҚТАУДЫ ҚАРАШЫҒАНАҚ ИННОВАЦИЯЛЫҚ ӘДІСІ - TLC- FID АРҚЫЛЫ

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(FID) Flame Ionization Detector бөлек затардың иондауын датчигі бар, таңдаулы еріткіштері (жылжымалы фаза) арқылы жұқа қабатты сорғышта (тұрақты фаза - Chromarods - кремилік беті бар кварц шыбығы) сұйық заттардың бөлінуінде негізделген әдіс. КПО химия лабораториясы бір кезеңіне дымды мұнайдың үлгісін 5 заттарға SWARA квалификацияларымен (Saturated-Waxes-Aromatics-Resins-Asphaltenes) түзуі бөлінуінің жете алады.

КАРАЧАГАНАКСКИЙ ИННОВАЦИОННЫЙ МЕТОД ПРЯМОГО ОПРЕДЕЛЕНИЯ НАСЫЩЕННЫХ УГЛЕВОДОРОДОВ - СМОЛ- АРОМАТИЧЕСКИХ СОЕДИНЕНИЙ –ПАРАФИНОВ-АСФАЛЬТЕНОВ С ПОМОЩЬЮ TLC- FID

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Основанный на разделении жидких веществ на тонкослойном абсорбере (постоянная фаза - Chromarods – кварцевый прут с кремниевой поверхностью) посредством селективных растворителей (подвижная фаза) комбинированный с датчиком ионизации отделенных веществ - Flame Ionization Detector (FID). Химическая лаборатория КПО может достигнуть прямого разделения образца сырой нефти за одну стадию на 5 веществ, квалифицированных как SWARA (Saturated-Waxes-Aromatics-Resins-Asphaltenes)

УДК 66.097

ПРИГОТОВЛЕНИЕ И ИССЛЕДОВАНИЕ КАТАЛИЗАТОРА В ВИДЕ ОКСИДА ЦЕРИЯ (IV) НА КЕМЕРТУЗСКОЙ ГЛИНЕ

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Предложена технология приготовления катализатора из оксида церия на носителе из глины Кемертузского месторождения, приготовленной в виде пористой керамики методом выгорающих добавок. Проведено сравнение с результатами окисления CO и CxHy на палладиевом катализаторе на Келесской глине.

Первые автомобильные нейтрализаторы были оснащены катализаторами, носители которых традиционно изготавливались в виде гранул из материала в виде оксида алюминия. Такие катализаторы хорошо освещены в монографиях Н.М. Поповой [2].

В нынешнее время, к нейтрализаторам, в соответствии и к носителям предъявляются следующие жесткие требования:

- активность и стабильность в широком интервале температур 200-800°С
- низкое гидродинамическое сопротивление;