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TAR MAHSULOTASOSIDA NEFT POLIMERQATRON OLISHKINETIKASI VA JARAYON SAMARADORLIGINI OPTIMALLASHTIRISH

Annotatsiya

Ushbu tadqiqot gaz-kimyo majmualarini qayta ishlash jarayonida hosil bo‘ladigan TAR mahsulotidan piroliz jarayonida havo miqdorini aniq o‘lchash va uni bosqichma-bosqich yetkazib berish orqali qatron ajratish jarayonini optimallashtirish, havo ishtirokida piroliz qilish, jarayonning kinetikasini taxlil qilishga orqali iqtisodiy va ekologik jihatdan xavfsiz mahsulotlarga aylantirishning innovatsion yondashuvlarini ilgari suradi. Natijalar qatron tarkibida aromatik birikmalar, reaktiv funksional guruhlar va tarmoqlangan uglerod zanjirlarining mavjudligini ko‘rsatdi. Arrenius tenglamasi asosida reaksiya uchun aktivlanish energiyasi (Ea) va kinetik tezlik doimiysi (k) hisoblab chiqildi. Bu jarayonning energiyaga bo‘lgan ehtiyojini aniqlash va uning samaradorligini baholash imkonini berdi.

Kalit so‘zlar: Ikkilamchi TAR mahsulotlari, qatron, piroliz, kinetika, Arrenius tenglamasi, termoliz, degidrogenlash, kislorod miqdori, optimal harorat.

OPTIMIZATION OF KINETICS AND PROCESS EFFICIENCY OF PETROLEUM POLYMER RESIN PRODUCTION BASED ON TAR PRODUCT

Annotation

This study proposes an innovative approach for optimizing the resin separation process from TAR products generated in gas-chemical complexes by accurately measuring and gradually supplying oxygen during pyrolysis. Pyrolysis in the presence of oxygen was analyzed kinetically to convert raw materials into economically and environmentally safe products. Based on the Arrhenius equation, the activation energy (Ea) and reaction rate constant (k) were calculated, allowing for the evaluation of energy requirements and process efficiency.

Keywords*:* Secondary TAR products, resin, pyrolysis, kinetics, Arrhenius equation, thermolysis, dehydrogenation, oxygen content, optimal temperature.

Kirish. Ikkilamchi TAR tarkibida fenollar, poliaromatik uglevodorodlar, asfaltenlar bo‘lib, ular yuqori energiya salohiyatiga ega xomashyodir [1-3]. TARning pirolizi nafaqat energiya manbai, balki qimmatbaho kimyoviy reagentlar kreking gazlari va qatronlarni olish uchun muhim texnologiya hisoblanadi [4-6]. Qatron miqdorining yuqori bo‘lishi va harorat oshgan sari kamayishi, degidrogenlash va polimerlanish jarayonlarining termodinamik aktivlanishi bilan izohlanadi [7-8]. 250–450 °C va 450–700 °C haroratda olib borilgan piroliz jarayonlari kinetik parametrlar Coats–Redfern modeli asosida tahlil qilingan bo‘lib, F1 kinetik modeli orqali aktivlanish energiyasi aniqlangan [9]. Avtomobil shinalari uchun kinetik ko‘rsatkichlar taqqoslangan va aktivlanish energiyasi mos ravishda 152 kJ/mol va 163 kJ/molni tashkil etgan. Kinetik tahlilda KAS, FWO va Friedman modellari qo‘llanilib, ΔG, ΔS va ΔH kabi termodinamik parametrlar tahlil qilingan.Unga ko‘ra, H_2 uchun Ea 72.9 kJ/mol, CH_4 uchun 43.9 kJ/mol, CO_2 uchun 18.5 kJ/mol va CO uchun 13.4 kJ/molni tashkil etadi [10-11]. Piroliz jarayonida havo miqdorini 15–30 mg/L oralig‘ida qo‘shib turish degidrogenlash va qisman oksidlanish reaksiyalarini faollashtiradi. Bu jarayonda aromatik strukturalar to‘g‘ri shakllanib, qatronning zichligi va tozaligi oshadi. Tanlangan havo miqdori reaksiya muvozanatiga ta’sir qilmaydigan darajada bo‘lib, radikal jarayonlarni samarali boshqarish imkonini beradi [12–14].

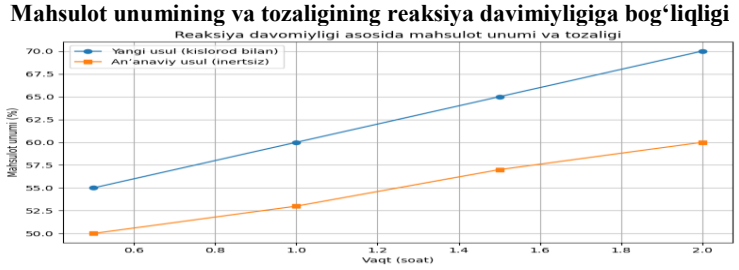
Tadqiqotning metodologiyasi. Ustyurt gaz-kimyo majmuasida piroliz jarayonida hosil bo‘ladiganzichligi 0.98 g/sm³, qaynash harorati 280–400 °C, aromatik uglevodorodlar miqdori 60 %, vodorod-uglerod nisbati (H/C) = 1.1.bo‘lgan TAR mahsulotidan foydalanildi. Kinetik tahlil va reaksiya tezligi ko‘rsatkichlari Arrenius tenglamasi orqali hisoblandi.Tajriba jarayonida xomashyo piroliz reaktoriga joylashtirilib, ikki xil sharoitda havo ishtirokidagi va an’anaviy usul asosida amalga oshirildi. Har ikki sharoitda reaksiya davomiyligi bo‘yicha namunalar 30 daqiqa, 1 soat, 1,5 soat va 2 soat oralig‘ida olindi.

Natijalar muhokamasi. Ustyurt gaz-kimyo majmuasi TAR mahsuloti piroliz jarayoni yangicha usulda havoni 15–30 mg/L miqdorda, bosqichma-bosqich kiritilishi orqali amalga oshirildi. Jarayon davomida oksidlanish reaksiyalari faollashib, fenollar va kislorodli funksional guruhlarning saqlanib qolishiga imkon yaratdi. Bu esa hosil bo‘lgan qatron mahsulotining tarkibi va fizik-kimyoviy xususiyatlarining yaxshilanishiga olib keladi. Havoning kam miqdorda reaksiya muhitiga kiritilishi radikal jarayonlarni samarali boshqarib, aromatik birikmalarning ajralib chiqish samaradorligini oshiradi, qatron mahsulotining zichligi va tozalik darajasining ancha yuqori bo‘lib past aktivlanish energiyasi sharoitida organik moddalarning to‘liq termolizlanishiga erishildi.

Ushbu xomashyoni piroliz orqali tarkibiy qismlarga ajratish jarayonida harorat, vaqt va reaksiya muhiti muhim omillar hisoblandi (1-rasm).

1-rasm

Mahsulot unumining va tozaligining reaksiya davimiyligiga bog‘liqligi

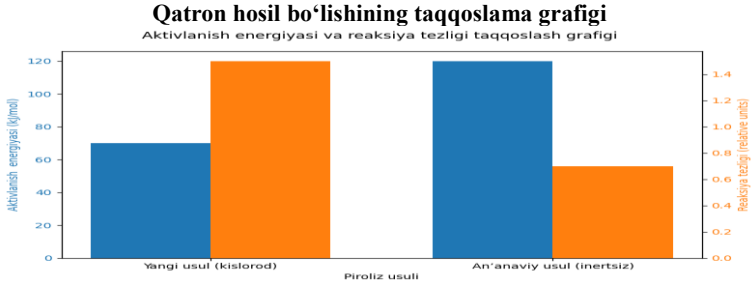


Grafikdan ko‘rinib turibdiki**,** sistemaga bosqichma-bosqich havo kiritish orqali qatron hosildorligi har bir vaqt oralig‘ida sezilarli darajada yuqori bo‘lgan. Reaksiya davomiyligi 2 soat bo‘lganda, mahsulot unumdorligi an’anaviy muhitda 60%, havo sharoitda esa 70 % ni tashkil etganini kuzatish mumkin.Bundan tashqari, piroliz jarayonida aktivlanish energiyasi va reaksiya tezligi kabi kinetik samaradorlik ko‘rsatkichlari ham tahlil qilindi. Havo muxitida va an’anaviy muhitdagi usullar o‘rtasidagi farqlar o‘rganildi. (2-rasm).

Grafikdan ko‘rinib turibdiki, kislorod ishtirokida TAR mahsuloti tarkibidan qatron ajratib olishda aktivlanish energiyasi Ea ≈ 70 kJ/mol bo‘lib, bu ko‘rsatkich an’anaviy usulda Ea ≈ 120 kJ/mol ga teng bo‘lgan. Shuningdek, reaksiya tezligi havo sharoitda **v** ≈ 1.5 ni tashkil etgan.

2-rasm

Qatron hosil bo‘lishining taqqoslama grafigi



Qatron ajratish jarayonida havo miqdorini aniqlash va yetkazib berishda jarayonning dastlabki 30 daqiqasida inert gazlarni siqib chiqarish va oksidlanish reaksiyalarini initsiatsiyalash maqsadida havoning o‘rtacha konsentratsiyasi 10–20 mg/l da berildi. Jarayonning 0.5-1,5 soatgacha bo‘lgan bosqichida asosiy oksidlanish reaksiyalari faollashishi sababli havo miqdori 20–50 mg/l gacha oshirildi. Piroliz jarayonida sodir bo‘ladigan organik moddalarning transformatsion reaksiyalarini quyidagi tartibda izohlash mumkin:

Termoliz reaksiyasi: molekulalarning yuqori harorat ta’sirida kichikroq birikmalarga parchalanib, uzun zanjirli uglevodorodlar qisqaroq zanjirli uglevodorodlarga va qatronga ajraladi.

$R{-}CH_2{-}CH_2{-}R'$ 300−400 ^0C $R{-}CH_3{+}R'{-}CH_3$+Qatron

2.Alkan va sikloalkanlarning vodorod atomlari ajralib chiqishi natijasida aromatik uglevodorodlarga aylanishi ya’ni degidrogenlanish:

$C_6H_{12} \rightarrow C_6H_6{+}3H_2$

3.Kislorodli funksional guruhlar, karboksil guruhlari parchalanib, transformatsion o‘zgarishlarga uchraydi va karbon kislotalardan karbonat angidrid hamda uglevodorodlar ajralib chiqadi.

$R{-}COOH \rightarrow CO_2{+}R{-}H$+Qatron

4.Shuningdek, piroliz jarayoni asosida qatron olish jarayonining muhim va so‘nggi bosqichlari bu kondensatsiyalanish va polimerlanish reaksiyalari bo‘lib, murakkab poliaromatik tuzilishli qatronlarni hosil qiladi.

5.$Ar{+}Ar'\cdot \rightarrow Ar{-}Ar'$(poliaromatik birikma)

Piroliz reaksiyalari odatda bir necha bosqichli reaksiyalar hamda qatronsimon moddalarning shakllanishi bilan boradi.

1-jadval

Piroliz jarayonining reaksiya kinetikasi

Reaksiya turlari	**Kimyoviy tavsifi**	**Misollar**
Bog‘ uzilishi	C–C, C–H va boshqa bog‘larning uzilishi	$R{-}CH_2{-}CH_2{-}R' \rightarrow R\cdot{+}\cdot CH_2{-}CH_2{-}R$
Radikallar tarqalishi	Organik radikallar hosil bo‘lishi	$R\cdot{+}R'H \rightarrow RH{+}R'$
Degidrogenlanish	Vodorod atomlarining ajralishi	Sikloalkan$\rightarrow$Arugedorod$+H_2$
Kondensatsiya va polimerlanish	Radikallar birikishi, molekulalarni hosil qilishi	$2R\cdot \rightarrow R{-}R$

Ikkilamchi piroliz mahsulotlaridan ajratib olingan ayrim organik birikmalarning vaqtga bog‘liq ravishda mahsulot unumi tahlil qilinib Arrenius tenglamasi yordamida kinetik parametrlar aniqlandi.

Arrenius tenglamasi: $k{=}A{\cdot}e^{-\frac{Ea}{RT}}$:

Reaksiyasi tezligi va kinetik parametrlarni aniqlashda dastlab bir guruh modda uchun reaktsiya kinetikasi birinchi tartibli deb hisoblanadi:

$$\frac{dC}{dt} = -kC \rightarrow C = C_{0e}^{\ -kt}$$

Yoki, agar chiqarilgan mahsulot miqdorini Y(t) desak:

$$Y\ (t) = Y\infty\dot{(}1 - e^{-kt})$$

Dastlab hisoblashlar fenollar va krezoqlar quyidagi unumlari (30-35 %, 25-30 %, 20-25 %) asosida mahsulot unumlari o‘rtacha qiymatlari quyidagi tartibda Y(2)=32.5, Y(4)=27.5, Y(6)=22.5 ga va uchala qiymat asosida maksimal chiqish unumi (Y∞) taxminan ≈35 % ga deb olamiz.

2. Arrenius tenglamasini to‘g‘ri qo‘llash uchun haroratni Kelvinga aylantiramiz.

T=275^{0}C=548.15 K(o‘rtacha 250–300 ^{0}C):

Eksel yoki regressiya orqali ***k*** ni topish

$$Y(t) = Y_\infty\,(1 - e^{-kt}) \rightarrow e^{-kt} = 1 - \frac{Y(t)}{Y\infty} \rightarrow k = \ln\ 1 - \frac{Y(t)}{Y_\infty} \rightarrow k = -\frac{1}{t}\ln\ \ 1 - \frac{Y(t)}{Y_\infty}$$

Fenollar uchun hisoblashlar:

$$k_{2h} - \frac{1}{2}\ln\ \ 1 - \frac{32.5}{35} = \ -\frac{1}{2}\ln(1 - 0.9286) = -\frac{1}{2}\ln(0.0714) = \frac{1}{2} * 2.639 = 1.3195$$

$$k_{4h} - \frac{1}{4}\ln\ \ 1 - \frac{27.5}{35} = \ -\frac{1}{4}\ln(0.214) = -\frac{1}{4} * 1.540 = 0.385$$

$$k_{6h} - \frac{1}{6}\ln\ \ 1 - \frac{22.5}{35} = \ -\frac{1}{6}\ln(0.357) = -\frac{1}{6} * 1.029 = 0.1715$$

Bu yerda mahsulot 2 soatda yuqori unum bilan chiqishi, keyingi soatlarda esa kamayishini inobatga olib, boshqa model yoki teskari reaksiya ham bor bo‘lishi mumkin.Arrenius tenglamasi orqali *Ea* ni aniqlash (ikki *k*, ikki *T* bo‘yicha) amalga oshiriladi.

$$ln\frac{k_2}{k_1} = \frac{E_a}{R}\frac{1}{T_1} - \ \frac{1}{T_2}$$

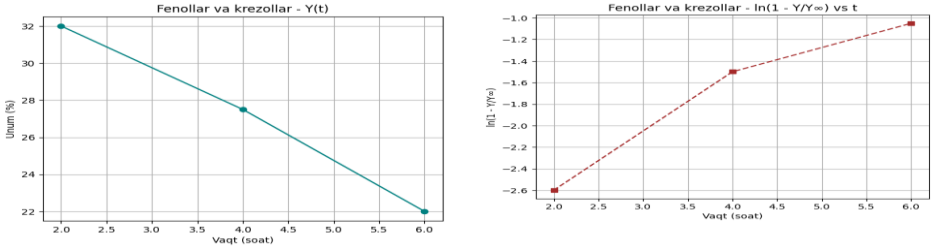
Agar 250°C (523.15 K) va 300°C (573.15 K) uchun k ma’lum bo‘lsa, shu usulda *Ea* aniqlanadi. Reaksiya harorati 250–300 °C oralig‘ida olib borilayotganligini inobatga olamiz, ya’ni:

$$\mathrm{T} = \frac{250 + 300}{2} = 275^0C = 548.15\ K$$

Belgilangan haroratda, turli vaqtda ajralib chiqqan moddalar miqdoriga asoslanib reaksiya tezligi konstantasi *k* va aktivlashtirish energiyasi *Ea* ni hisoblab topamiz (3-4-rasm).

3,4-rasm

Reaksiya tezligi konstantasi k va aktivlanish energiyasi



1.Maksimal unumY∞≈35%

2. Tezlik konstantasini topish uchun 1-tartibli kinetika tenglamasidan foydalanamiz.

$$Y(t) = Y_\infty(1 - e^{-kt}) \rightarrow k = -\frac{1}{t}\ln\ \ \ \ 1 - \frac{Y(t)}{Y_\infty}$$

Hisoblashni quyidagi tartibda olib boramiz.

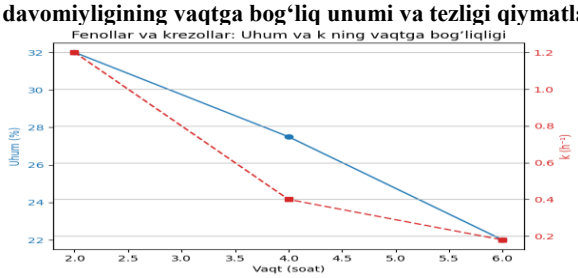
t=2 соат $k_2 = -\frac{1}{2}\ln\ \ 1 - \frac{32.5}{35} = -\frac{1}{2}\ln\,(0.0714) = \frac{1}{2} *\ 2.639 = 1.3195\ \mathrm{h}^{-1}$

t=4 соат $k_4 = -\frac{1}{4}\ln(1 - \frac{27.5}{35}) = -\frac{1}{4}\ln\,(0.2143) = \frac{1}{4}\ *\ 1.540 = 0.385\ \mathrm{h}^{-1}$

t=6 соат $k_6 = -\frac{1}{6}\ln(1 - \frac{22.5}{35}) = -\frac{1}{6}\ln\,(0.357) = \frac{1}{6}\ *\ 1.029 = 0.1715\ \mathrm{h}^{-1}$

5-rasm

Reaksiya davomiyligining vaqtga bog‘liq unumi va tezligi qiymatlari grafigi

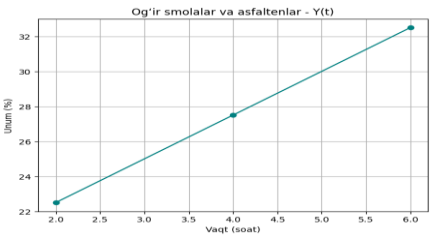


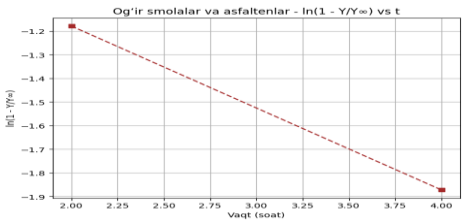
Xulosa qilib aytishimiz mumkinki, jarayonda k kamayib boradi, bu esa reaksiya sur’ati vaqt o‘tishi bilan pasayishini ko‘rsatadi. Smolalar va aromatik uglevodorodlar uchun ham reaksiya tezligi k ni hisoblaymiz. Harorat – 275°C = 548.15 K, va reaksiya birinchi tartibli deb hisoblaymiz.

$$Y(t) = Y_\infty(1 - e^{-kt}) \rightarrow k = -\frac{1}{t}\ln\ \ \ \ 1 - \frac{Y(t)}{Y_\infty}$$

6,7-rasm

Og‘ir smolalar va asfaltenlarning vaqtga bog‘liqlik grafigi





Maksimal unum Y∞≈35%

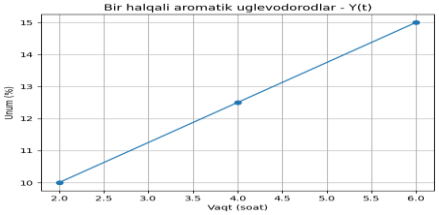
t=2 соат $k_2 = -\frac{1}{2}\ln\ 1 - \frac{22.5}{35} = -\frac{1}{2}\ln(0.3571) = \frac{1}{2} * 1.029 = 0.5145\ \mathrm{h}^{-1}$

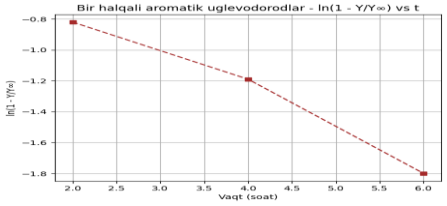
t=4 соат $k_4 = -\frac{1}{4}\ln(1 - \frac{27.5}{35}) = -\frac{1}{4}\ln(0.2143) = \frac{1}{4} * 1.540 = 0.385\ \mathrm{h}^{-1}$

t=6 соат $k_6 = -\frac{1}{6}\ln(1 - \frac{32.5}{35}) = -\frac{1}{6}\ln(0.714) = \frac{1}{6} * 2.639 = 0.4398\ \mathrm{h}^{-1}$

8-9rasm

Bir halqali aromatik uglevodorodlarining hosil bo’lish ununing vaqtga bog’liqligi





Maksimal unum Y∞≈18%

t=2 соат $k_2 = -\frac{1}{2}\ln\ 1 - \frac{10}{18} = -\frac{1}{2}\ln(0.444) = \frac{1}{2} * 0.813 = 0.4065\ \mathrm{h}^{-1}$

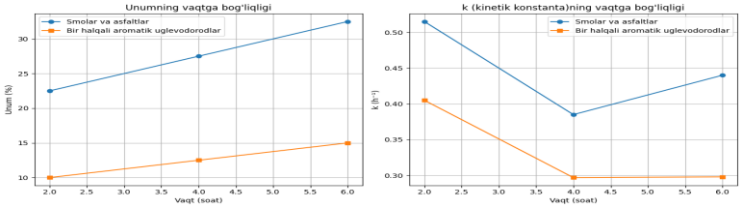
t=4 соат $k_4 = -\frac{1}{4}\ln(1 - \frac{12.5}{18}) = -\frac{1}{4}\ln(0.3056) = \frac{1}{4} * 1.186 = 0.2965\ \mathrm{h}^{-1}$

t=6 соат $k_6 = -\frac{1}{6}\ln(1 - \frac{15}{18}) = -\frac{1}{6}\ln(0.1667) = \frac{1}{6} * 1.792 = 0.2987\ \mathrm{h}^{-1}$

Smolalar, asfaltenlar va bir halqali aromatik uglevodorodlar hosil bo‘lishida unumnng hamda reaksiya kinetikasi konstantasining vaqtga bog‘liqlik grafigi ishlab chiqildi.

10-11rasm

Reaksiya kinetikasi konstantasining vaqtga bog‘liqlik grafiki



Grafikga ko‘ra, vaqt 2 soatdan 6 soatga oshishida unum 10 % gacha ortib, smolalar va asfaltenlarning konversiyasi oshib bormoqda. K (kinetik konstanta) ning vaqtga bog‘liqligida esa 2 soatdan 4 soatgacha oshishi bilan K ning pasayishi, 6 soatga yetganda esa unum nisbatan ko‘tarilishi kuzatilgan.

Xulosa. Ikkilamchi piroliz mahsulotlarini havo ishtirokidagi oksidlash kinetikasi va qatron olish samaradorligi o‘rganildi va piroliz samaradorligi 25-30% ga oshirildi. Reaksiya aktivlanish energiyasi 15-20 kJ/mol ga kamayib, tezligi 1.5-2 marta oshdi, bu esa energiya samaradorligi va mahsulot chiqimiga ijobiy ta'sir ko‘rsatdi. Reaksiya davomiyligi 2 soat bo‘lganda, mahsulot unumi havo mixitida 60 %, an’anaviy sharoitda esa 70% ni tashkil etdi. Arrhenius tenglamasi asosida reaksiya kinetik parametrlari aniqlandi, va tezlik doimiylari hisoblandi. Umuman, havo ishtirokidagi yangi usul nafaqat ekologik jihatdan xavfsiz va energiya tejamkor, balki yuqori sifatli qatron olishda samarali va iqtisodiy jihatdan maqbul texnologiya sifatida e'tirof etildi.

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